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THE INFLUENCE OF CHEMICAL REACTIONS ON THE MOBILITY OF RADIONUCLIDES IN THE TERRESTRIAL ENVIRONMENT

Lars Carlsen, Ole John Nielsen, Peter Bo, and Conny Ditlevsen

Abstract. The influence of the kinetics of chemical and physico-chemical reactions on the mobility of radionuclides in the terrestrial environment has been studied theoretically by application of the COLUMN2 computer code. A variety of reaction systems has been analyzed comprising:

$A \rightarrow B$

$A \rightarrow B \rightarrow C$

$A \rightleftarrows B$

$A \rightleftarrows B \rightarrow C$

$A \rightleftarrows B \rightleftarrows C$

$A + X \rightarrow B$

$A + B \rightleftarrows C$

$A + B \rightleftarrows C + D.$

The study unequivocally discloses the importance of the chemistry in controlling the migration behaviour of contaminants, e.g. radionuclides in the terrestrial environment. The analyses suggest the necessity of studying possible geochemical reaction in detail, including both retention characteristics as well as reaction kinetics.

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1. INTRODUCTION

When radionuclides are released to the ground water and subsequently transported in the liquid phase of the terrestrial environment, a wide variety of chemical and physico-chemical reactions can a priori be expected to occur. The processes comprise e.g. radioactive decay, sorption/desorption, precipitation/dissolution, redox equilibria, degradations, substitution, hydrolysis, complex formation, and colloid formation. All these types of reactions as well as changes in the ground water composition have to be taken into account, since they may play an important role in determining the migration behaviour of the radionuclides.

In nature a complicated interplay between different reactions, eventually determining the migration behaviour of trace elements, most probably takes place. The aim of the present study is not to describe the effect of highly sofisticated combinations of the above mentioned reactions, although it can be done, but through selected examples to elucidate the possible significance of certain parameters.

The investigations have been carried out theoretically by application of the COLUMN2 computer code (Nielsen, Carlsen, and Bo, 1985), which gives a one-dimentional description of the migration phenomena taking arbitrarily chosen chemical/physico-chemical processes into account. COLUMN2 is a revised version of the orginal COLUMN program, which appeared in 1978 (Bo, 1978). The basic mathematical description applied in COLUMN2 (Nielsen, Carlsen, and Bo, 1985) is reproduced in the following section.

2. MATHEMATICAL DESCRIPTIONS

2.1. Convection and dispersion

Common to all the solutes present in the liquid phase is the transport due to convection and dispersion which we describe by:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - V \frac{\partial c_i}{\partial x} \qquad (1)$$

where c_i is the concentration of component i.

D_i is the dispersion coefficient of component i.

V is the interstitial velocity of the liquid phase ($V = q/\varepsilon$)

q is the volume flow per unit crossectional area.

ε is the porosity (volume fraction of liquid) of the porous medium.

t is the time.

x is the length coordinate.

Equation (1) assumes that neither the dispersion nor the interstitial velocity changes in the x-direction. Most often the interstitial velocity will be so high that all components have the same dispersion coefficient, but at very low velocities differences between the individual components do occur as a result of their individual diffusion coefficients in the liquid phase.

It sometimes happens that it is necessary to account for a component that does not move with the fluid flow, e.g. precipitates and absorption in the solid phase under non-equilibrium conditions. This can be done by setting the dispersion coefficient and the interstitial velocity equal to zero for such components.

2.2. Equilibrium adsorption/absorption phenomena

2.2.1. General description

When, in addition to dispersion and convection, components are transferred between the liquid (flowing) and the solid (stationary) phases, the transport equation (1) is modified by adding a term which describes the effect of these processes on the concentration in the liquid phase:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - V \frac{\partial c_i}{\partial x} - \frac{\varepsilon_s}{\varepsilon} \frac{\partial \bar{c}_i}{\partial t} \qquad (2)$$

where $\bar{c}_i$ is the concentration of i in the solid phase, and ε_s is the volume fraction of the solid phase. If the process is an adsorption on a surface, ε_s and $\bar{c}_i$ has the meaning of specific surface area and surface concentration, respectively.

2.2.2. Ion Exchange

Ion exchange is one of the more important mechanisms by which positively charged ions are retained in soil. The exchange process is relatively rapid and reversible. Therefore the assumption of maintaining equilibrium at all times during the migration is most often fulfilled.

The equilibrium is determined by the equality of the electrochemical potentials in the ion exchange phase and in the liquid phase for each of the components present. Expressed in terms of concentrations this equilibrium can be written:

$$\bar{c}_i = c_i \frac{\gamma_i}{\bar{\gamma}_i} K_i \, Z^{z_i/\omega} \qquad (3)$$

where

$$Z = \exp(\omega F(\psi - \bar{\psi})/RT) \tag{4}$$

$$K_i = \exp((\mu_i^o - \bar{\mu}_i^o)/RT) \tag{5}$$

and γ_i is the activity coefficient of component i
z_i is the valence factor of the component i
ω is the charge factor for the fixed ions in the exchange phase (-1 for a cation exchanger)
μ_i^o is the standard chemical potential of component i
ψ is the electrical potential of the phases
F is Faradays number
R is the gas constant
T is the absolute temperature
a bar ($^-$) over a symbol refers to a property in the ion exchange phase.
K: distribution coefficient
Z: potential function

Z is determined by the condition of electroneutrality in the ion exchange phase:

$$\sum_j z_j \bar{c}_j + \omega X = o \tag{6}$$

where X is the concentration of the fixed ionic groups in the exchanger phase. Inserting (3) in (6) gives a polynomial expression in Z which can be solved when the constants and the concentrations in the liquid phase are known.

With the above expressions for the equilibrium we find:

$$\frac{\partial \bar{c}_i}{\partial t} = K_i \frac{\gamma_i}{\bar{\gamma}_i} Z^{z_i/\omega} \frac{\partial c_i}{\partial t} + \frac{z_i}{\omega} c_i K_i \frac{\gamma_i}{\bar{\gamma}_i} Z^{z_i/\omega} \frac{\partial \ln Z}{\partial t}$$

which with

$$K_{Di} = K_i \frac{\gamma_i}{\bar{\gamma}_i} Z^{z_i/\omega} \tag{7}$$

gives

$$\frac{\partial \bar{c}_i}{\partial t} = K_{Di} \frac{\partial c_i}{\partial t} + \frac{z_i}{\omega} c_i K_{Di} \frac{\partial \ln Z}{\partial t} \tag{8}$$

When inserted into the migration Eq. (2) with

$$A_i = 1 + K_{Di} \frac{\varepsilon_s}{\varepsilon} \tag{9}$$

where A_i is inverse retention factors, we get

$$\frac{\partial c_i}{\partial t} = \frac{D_i}{A_i} \frac{\partial^2 c_i}{\partial x^2} - \frac{v}{A_i} \frac{\partial c_i}{\partial x} - c_i \frac{A_i^{-1}}{A_i} \frac{\partial \ln Z}{\partial t} \tag{10}$$

in which

$$\frac{\partial \ln Z}{\partial t}$$

can be expressed in terms of

$$\frac{\partial c_j}{\partial t}$$

through

$$\frac{\partial \ln Z}{\partial t} = \sum_i \frac{1}{Z} \frac{\partial Z}{\partial c_j} \frac{\partial c_j}{\partial t}$$

or using the electroneutrality condition in the form

$$\sum_j z_j \frac{\partial \bar{c}_j}{\partial t} = 0 \ .$$

The microchemistry, i.e. the components that need not be considered when calculating Z, can often be described by the simplified equation:

$$\frac{\partial c_i}{\partial t} = \frac{D_i}{A_i} \frac{\partial^2 c_i}{\partial x^2} - \frac{v}{A_i} \frac{\partial c_i}{\partial x} \qquad (11)$$

However, this requires that either the macro-chemistry and therefore Z is independent of time or A_i is very close to 1.

Finally it should be mentioned that neither Z nor the individual K_i's are thermodynamically well defined and should, in actual calculation, be replaced by products and ratios of these parameter that are thermodynamically well defined.

2.2.3. Other types of sorption

When the sorption isotherm is known:

$$\bar{c}_i = f_i(c_j, \ldots\ldots)$$

as a function of all components present, the time derivative can be found

$$\frac{\partial \bar{c}_i}{\partial t} = \frac{\partial f_i(c_j, \ldots.)}{\partial c_1} \frac{\partial c_1}{\partial t}$$

Defining $K_{Di} = \dfrac{f_i(c_j, \ldots..)}{c_i}$ and $A_i = 1 + \dfrac{\varepsilon_s}{\varepsilon} K_{Di}$ (12)

We get the transport equation:

$$\frac{\partial c_i}{\partial t} = \frac{D_i}{A_i}\frac{\partial^2 c_i}{\partial x^2} - \frac{v}{A_i}\frac{\partial c_i}{\partial x} + \frac{A_i - 1}{A_i}\frac{\partial c_i}{\partial t}$$

$$- \frac{\varepsilon s}{\varepsilon} \sum_l \frac{\partial f_i(c_j,....)/\partial c_l}{A_i}\frac{\partial c_l}{\partial t} \qquad (13)$$

This again takes the form (13) if for all $l \neq i$ either

$$\frac{\partial f_i(c_j,....)}{\partial c_l} = 0 \text{ , or } \frac{\partial c_l}{\partial t} = 0 \text{ , and for } l = i$$

$$\frac{\partial f_i(c_j,....)}{\partial c_i} = \frac{f_i(c_j,.....)}{c_i} \text{ .}$$

The first and last condition is likely to hold true for many microcomponents whereas the second will sometimes be a good approximation for macrocomponents.

2.3. Chemical reactions in solution and radioactive decay

Homogeneous chemical reactions and that part of heterogeneous reactions that concerns dissolved species and radioactive decay

are introduced into the transport equation by adding terms of the form

$$\sum_l \prod_j S_{ij}^l \, c_j^{a(l,j)}$$

where l represents the chemical reaction in question and j is a component in this reaction which enters the reaction rate for component i with the coefficient S_{ij}^l and the exponent a(l,j).

For first order reactions and radioactive decay the above expression simplifies to

$$\sum_{1} S_{il}\, c_l$$

since, in this case, the reaction can be identified with the component involved in the reaction. This expression gives a transport equation of the form:

$$\frac{\partial c_i}{\partial t} = \frac{D_i}{A_i}\frac{\partial^2 c_i}{\partial x^2} - \frac{V}{A_i}\frac{\partial c_i}{\partial x} + \sum_{1}\frac{S_{il}}{A_i} \qquad (14)$$

in which also retention due to sorption, in its simplest form, has been taken into account.

Since

$$S_{il} = \left(\frac{\partial c_i}{\partial t}\right)^{1}\frac{1}{c_l} \qquad (15)$$

where the superscript 1 means that part of the derivative that is due to the reaction 1, S_{il} is, for a simple chemical reaction, a normal rate constant.
For radioactive decay, which is going on both in the liquid and in the solid phase

$$S_{il} = \lambda_1 + \lambda_1 \frac{\varepsilon_s}{\varepsilon} K_{D1} = \lambda_1 A_1 \qquad (16)$$

where λ_1 is the decay constant - taken positive for parent radionuclides ($1 \neq i$) and negative for the component i itself.

The two terms in the middle part of (16) arises because of decay in the liquid phase and of reestablishing of equilibrium between and solid phase-following decay in the solid phase.
An other important application of these equations is to pseudo-first order reactions in which e.g. a complexing agent (L^{z_l}) reacts with positively charged ions (M^{z_m}) to form another charged species

$$M^{z_m} + L^{z_l} \rightleftharpoons ML^{z_m+z_l} \qquad (17)$$

with a retention (A_i) different from the simple ion. When the concentration of the complexing agent is high compared to the concentration of the ion M^{z_m}, the reactions (17) can be treated as first order reactions. Hydrolysis and precipitation of micro-components in buffered system or when the concentration of the precipitating component is high compared to the concentration of the microcomponent can also, at least to a certain extent, be treated as first order reactions.

The second order reactions are not introduced directly into the transport equation but treated seperately. Terms of the form

$$S2^l_{ij} \times c_i \times c_j \times dt$$

are subtracted and added, respectively, to the concentrations of the relevant components for each reaction, r, where

$S2^l_{ij}$ is the second order rate constant of the reaction l
c_i is the concentration of the reactant i
c_j is the concentration of the reactant j.

3. NUMERICAL METHODS

A finite difference explicite algorithm has been chosen. Using the method of characteristics, Eqs. (1) or (11) is rearranged thus:

$$\frac{dc_i}{dt} = \frac{\partial c_i}{\partial t} + \frac{V}{A_i}\frac{\partial c_i}{\partial x} = \frac{D_i}{A_i}\frac{\partial^2 c_i}{\partial x^2} \qquad (18)$$

where the substantial derivative on the left is the concentration change in a local liquid volume that follows the movement (V/A_i) of the component i in the liquid phase. In this way the stability problem with the otherwise hyperbolic equation is circumvented - but it necessitates the introduction of a set of grid points (space points at which concentrations etc. are calculated) that are moving with the velocity V/A_i relative to the stationary phase - i.e. the column. This gives the following integration cycle:

1) Calculate the concentrations at the fixed grid points from the values at the moving points. This is done by averaging over flowing grid points that are within half a fixed grid point interval form a given fixed grid point.
2) Perform the numerical integration on the equidistant fixed grid points.
3) Calculate the new concentrations on the moving grid points by adding the increement found in 2) for each of the fixed grid points, to all the moving grid points within half a fixed grid point interval from the given fixed grid point.
4) Move the flowing grid points by adding to their corresponding x-values - V/A_i times the time increement.

This calculating procedure gives on the average very accurate results but has a tendency to give local (in space) errors when sharp concentration profiles on the moving grid points pass a fixed grid point.

The logical way to remove these difficulties is to dispense with the fixed grid points and perform the integration on the moving

grid points. This makes the integration cycle consist of only two operations:

1) perform the integration on the moving grid points
2) move the grid points by adding V/A_i times the time increement to their x-values, thus keeping track on the where abouts of the different components.

This necessitates an integration procedure that is able work with grid points that are not equidistant. Also one components concentration has to be calculated at other components grid points. This is done by interpolation.

The first order finite difference representation of first and second order partial differential coefficients for nonequidistant grid points, as used here, are:

$$(\frac{\partial c}{\partial x})_{x(L)} = c_L' = \frac{1}{2}\left(\frac{c_{L+1} - c_L}{h_{L^+}} + \frac{c_L - c_{L-1}}{h_{L^-}}\right) \qquad (19)$$

$$(\frac{\partial^2 c}{\partial x^2})_{x(L)} = c_L'' = \frac{2}{h_{L^+} + h_{L^-}}\left(\frac{c_{L+1} - c_L}{h_{L^+}} - \frac{c_L - c_{L-1}}{h_{L^-}}\right) \qquad (20)$$

Both reduce to first order central differences approximations for $h_{L+} = h_{L-}$ (cf. Nielsen, Carlsen, and Bo, 1985). For simplicity of exposition the component identification subscript has been omitted.

Using for the time derivative a foreward difference:

$$(\frac{dc}{dt})_{x(L)} = \frac{c_{L,n+1} - c_{L,n}}{k} \qquad (21)$$

where n enumerates the time and k is the time interval, and introducing the abreviation:

$$H = \frac{2\ h_{L-}}{h_{L^+} + h_{L^-}}$$

we get for the differential equation:

$$\frac{dc}{dt} = \frac{D}{A}\frac{\partial^2 c}{\partial x^2}$$

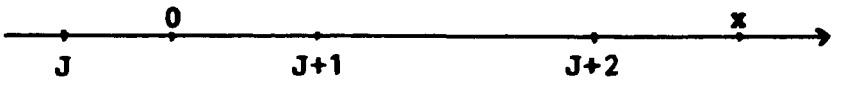
the explicite finite difference expression:

$$c_{L,n+1} = c_{L,n} + \frac{D \times k}{A \times h_{L^+} \times h_{L^-}} (H(c_{I+1,n} - c_{L,n}) -$$

$$(2-H)\ (c_{L,n} - c_{L-1,n})) \qquad (22)$$

from which the concentration profile at time (n+1)k can be calculated from the profile at time n+k.

At the boundary x=0, the input concentration to the column must be specified as function of time i.e. $c_o = g(t)$. This is the mathematical boundary condition at this point. Since integration will be made between grid points normally, and since we cannot be sure whether we have a grid point at x=0 or not, the integration for the first point in the column, i.e. with X(I,J+1):



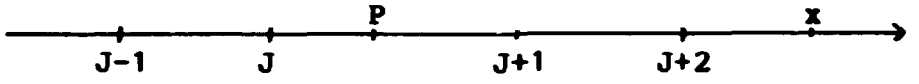
is made using (22) but substituting x=0 and c_o for the point at L-1.

At the end of the column of length P, i.e. at x=P the mathematical boundary condition is:

$$\left(\frac{\partial c}{\partial x}\right)_P = 0 \ .$$

Since we do not always have a grid point at x=P we have to make an interpolation:

$$c'_P = c'_J + (P - x_J)(c'_{J+1} - c'_J)/(x_{J+1} - x_J) = 0.$$



which results, using (19), in the following expression for $c_{J+2,n+1}$:

$$c_{J+2,n+1} = c_{J+1,n+1} - \frac{x_{J+2} - x_{J+1}}{P - x_J}(c_{J+1,n+1} - c_{J,n+1})$$

$$+ \frac{P - x_{j+1}}{P - x_J}\frac{x_{J+2} - x_{J+1}}{x_J - x_{J-1}}(c_{J,n+1} - c_{J-1,n+1}) \qquad (23)$$

This means that the normal integration using (22) must be carried out up to and including the grid point J+1.

For ion exchange and other equilibrium sorption phenomena A_i is calculated in a subroutine specially prepared for the specific problem at hand.

As seen from Eqs. (10) and (13) it is sometimes necessary to solve a set of partial differental equations that are coupled through their partial time derivatives (not through the substantial time derivatives). The correct way to solve this problem would be to solve the resulting m equations in m unknown partial time derivatives ($\partial c_i/\partial t$). Such a procedure does not fit into the general scheme used here, where only the substantial derivative is calculated. It is furthermore likely to give stability problems because of the mixed parabolic ($\partial^2 c_i/\partial x^2$) and hyperbolic ($\partial c_i/\partial x$) nature of the set of equations that result from considering the partial time derivatives as the unknowns.

An approximation that is numerically easier to handle is to substitute the value of the partial time derivatives that can be calculated from the known concentration profiles at time (n-1)×k and n×k - for the ones that appear on the right side of (10) and (13) and should correspond to the time internal n×k to (n+1)×k. This adds to the right side of (22), considered to describe the concentration of component i, a term of the form:

$$\sum_j Q_{ij} \times k \times (c_{j,x_i(L),n} - c_{j,x_x(L),n-1}) \qquad (26)$$

where the subscript "$x_i(L)$" means that the concentration of component j should be evaluated at this x-value which is a grid point for component i but most often not for component j when $j \neq i$. In the same way Q_{ij}, whose meaning depends on the specific problem to be solve, should be evaluated at the same place.

4. IMAGINABLE REACTIONS

As indicated in the introduction the behaviour of radionuclides in the environment may be a result of a complicated interplay between a variety of processes. However, in principle, all processes can be regarded as more or less sophisticated combinations of uni- and bimolecular reactions. In practice, on the other hand, the majority of bimolecular reactions will involve the macrocomponents in the ground water, the concentrations of these being up to several orders of magnitude higher than those of the microcomponents under investigation. Hence, these reactions can be treated as pseudo first-order reactions with respect to the micro components. In Table I the different elementary reactions that should be taken into account are summarized.

Table I. Characterization of elementary reactions, which may influence the migration. (FO: first-order, PFO: pseudo first-order, SO: second order)

Reaction	Type	Forward	Backward
Radioactive Decay Chains	$A \rightarrow B \rightarrow \cdots \rightarrow C$	FO	-
Sorption/Desorption	$A \rightleftarrows B$	FO	FO
Precipitation/Dissolution	$A \rightleftarrows B$	FO	FO
Redox Reactions[a]	$A \rightleftarrows B$	PFO	PFO
Degradations	$A \rightarrow \Sigma B_i$	FO	-
-	$A+X \rightarrow \Sigma B_i$	SO/PFO	-
Substitutions[b]	$A+X \rightarrow B$	SO/PFO	-
Hydrolysis	$A+OH \rightarrow B$	PFO	-
Complex Formation[c]	$A+L \rightleftarrows AL$	SO/PFO	FO
Colloid Formation[d]	$nA \rightarrow A_n$	SO	-

[a] The redox potential will generally be controlled by the macro composition of the ground water (e.g. by the Fe(II)/Fe(III) couple)

[b] The substitution reactions may be of importance in cases of organic pollutants

[c] In the case of complex formation, which can be expected to influence the migration behaviour of metal cations significantly, it is to be expected that in most cases it can be treated as a PFO reaction, owing to a large excess of the ligand, or a constant concentration of the latter (e.g. naturally occurring ligands in ground water).

[d] Colloid formation can in principle be regarded as a consecutive series of SO reactions.

Numerous combinations of the above mentioned elementary reactions can be imagined. Especially parallel reactions, e.g. as a result of concurring chemical and microbiological transformations, and consecutive reactions, e.g. hydrolysis subsequently followed by a precipitation/dissolution reaction of the hydrolysed species, can be mentioned.

In the following sections a series of imaginable reactions are treated to elucidate the influence of chemical reactions on the mobility of radionuclides in the terrestrial environment.

The investigated systems comprise, apart from the simple reference case, exhibiting one non-reacting species (react.-1), the following reactions sequences:

$A \rightarrow B$	react.-2
$A \rightarrow B \rightarrow C$	react.-3
$A \underset{\leftarrow}{\overset{\rightarrow}{}} B$	react.-4
$A \underset{\leftarrow}{\overset{\rightarrow}{}} B \rightarrow C$	react.-5
$A \underset{\leftarrow}{\overset{\rightarrow}{}} B \underset{\leftarrow}{\overset{\rightarrow}{}} C$	react.-6
$A + X \rightarrow B$	react.-7
$A + B \underset{\leftarrow}{\overset{\rightarrow}{}} C$	react.-8
$A + B \underset{\leftarrow}{\overset{\rightarrow}{}} C + D$	react.-9

In the single sections the influence of rate constants, i.e. reaction kinetics, and retention factors shall be discussed. In addition the 'possible chemistry' behind the reactions are to be mentioned.

It should be noted that throughout the report the amount of material transported by the liquid phase through the column is given in concentration units, i.e. mol m^{-3}. However, in connection with the risk assessment of geochemical barriers, one is generally concerned with total quantities, i.e. mass per unit

time, rather than concentration.

Since the flow velocity used in COLUMN2 is the interstitial velocity through the pores of the porous media, the total flow of a compound i, Q_i, through a cross section of the column is related to the concentration, c_i, simply by

$$Q_i = A_{eff} \times J_i = A_{eff} \times (-D\partial c_i/\partial x + Vc_i) \qquad (25)$$

where J_i is the flux through the effective cross section area, V is the interstitial velocity of the ground water (m y^{-1}) and A the geometrical cross scetion area of the column (m^2) under investigation. Hence, $A_{eff} = A \times \varepsilon$, ε being the porosity, denotes the effective cross section area, i.e. the cross section area of the liquid phase.

The total quantity transported through a cross section of the column during a period of t years, $Q_i(t)$ is then given by

$$Q_i(t) = \int_0^t A_{eff} \times J_i \times dt \qquad (26)$$

In all cases analyzed in the following sections (apart from section 4.7) identical input concentrations have been applied, i.e. the inputs consist of 2 m broad square pulses, the liquid phase concentrations being equal to 1 mol m^{-1}, started at the first point just outside the column. The total column lengths applied are 100 m.

All examples displayed are illustrated by two different types of plots, i.e. concentration plot and eluate plots. The first type visualizes the profiles of the liquid phase concentration throughout the column, typically displayed in 20 years intervals. The corresponding concentrations on the solid phase can indirectly be estimated via the distribution coefficient. The second type

of plots, elucidates the concentrations in the eluate, collected at the end of the column, as a function of time.*

4.1. A

The system illustrates the behaviour of a single non-reacting species in the ground water system, influenced by dispersion and sorption only. This could e.g. denote the behaviour of simple monovalent ions such as cesium.

Examination of this system discloses a series of fundamental features:

1° Increase in the retention factors causes concentration profiles throughout the column, to be 'delayed' proportionally to the R_f value. Relatively the peaks become broader by increased retention as the height, reflecting the concentration in the liquid phase, decreases by increased R_f values. Fig. 1-1, 1-2, and 1-3 visualize the effect, R_f being 1, 5, and 10, respectively (ground water velocity 1 m y^{-1}, dispersion coefficient 0.03 m y^{-2}). The corresponding elution curves, featuring a broadening proportional to the R_f value are depicted in Fig. 1-4.

2° Decrease in interstitial ground water velocity affords, for fixed R_f, a pronounced increased dispersion, due to time effects as seen by comparing Fig. 1-1 (V=1 m y^{-1}) and Fig. 1-5 (V=0.1 m y^{-1}). The effect is likewise reflected in the elution curve given in Fig. 1-6, which should be compared to that in Fig. 1-4.

3° The effect of a decrease in the dispersion coefficient is,

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* The 'SI-numbers' (e.g. SI301E) given on all plots are for internal classification purposses only.

not unexpected, a narrowing of the concentration profiles, i.e. a decreased dispersion. Comparing Fig. 1-7 ($D=0.003$ m y^{-2}) and Fig. 1-1 ($D=0.03$ m y^{-2}) visualizes the phenomenon. The corresponding elution curves are depicted in Fig. 1-8 and Fig. 1-4, respectively.

The following reaction systems will in all cases be studied for a ground water velocity $V=1$ m y^{-1} and a dispersion coefficient $D=0.03$ m y^{-2}, i.e. only the retention factors for the single components and the mutual interconvertion rate constants are changed.

4.2. A → B

The A → B system represents the irreversible conversion of A to B, which e.g. corresponds to the simple radioactive decay of A to its daughter nuclide B, e.g. Ra(226) → Rn(222). Also irreversible first order chemical (e.g. thermally or catalytically induced degradations) or microbial decay reactions are covered by this system.

The effect of variation in the rate constant, k_1, for the A → B reaction is illustrated in Fig.'s 2-1 through 2-4, depicting concentration profiles and elution curves for $k=0.1$ and 0.01 y^{-1}, respectively ($R_f(A)=R_f(B)=1$).

In cases where $R_f(A)$ or $R_f(B)$ is greater than 1, the concentration profiles of component A will, as a result of the irreversibility of the process be left unchanged (apart from simple migration phenomena), whereas pronounced tailing effects can be observed for component B. In cases where $R_f(A)<R_f(B)$ some B will be produced from A at positions where the B component has not yet reached, i.e. some B apparently moves faster than expected based on the value of the retention factor alone. On the other

hand, if $R_f(A)>R_f(B)$ some B will be produced at positions where the B component already has passed, i.e. some B apparently moves slower than expected from the $R_f(B)$ value. Fig.'s 2-5 through 2-8 visualize the effect on the concentration profiles and the elution curves, respectively, in case of a relatively rapid reaction ($k=0.1\ y^{-1}$). Decrease in conversion rate will eventually leade to a significant '<u>chemical dispersion</u>' of component B as illustrated by Fig. 2-9 through 2-12.

4.3. A → B → C

The A → B → C system denotes an irreversible reaction sequence, e.g. radioactive decay chains, as U(239) → Np(239) → Pu(239) or consecutive chemical decompositions. The trends observed for the A → B system are refound here, i.e. increased relative retention of one of the species results in chemical dispersion phenomena, the effect being significantly more pronounced when slow processes are involved. Concentration profiles for selected values of retention factors and rate constants are depicted in Fig.'s 3-1 through 3-12, the corresponding elution curves being shown in Fig.'s 3-13 through 3-24.

4.4. A ⇄ B

The more important type of reactions belonging to the A ⇄ B system is the redox equilibria, as e.g. $Tc^{VII}O_4^- \rightleftarrows Tc^{IV}$ or $Pu^{III} \rightleftarrows Pu^{IV}$. A variety of reports describing different migration behaviour of single elements in different oxidation states are available.

The reference case, i.e. the relative rapid equilibrium (here $k_1=k_2=0.1\ y^{-1}$) where none of the two species are retained, i.e. $R_f(A)=R_f(B)=1$ exhibits the expected behaviour as visualized in

Fig.'s 4-1 and 4-2, the latter being the elution curves, in which both A and B show up after 100 years.

Significant decrease in the rate constant k_1, i.e. A → B being slow, turned the system into the simple "A" system (cf. section 4.1.). On the other hand, in case of a slow B → A reaction, i.e. k_{-1} low, resulted in the "A → B" system as described in section 4.2.

In the case of a rapid equilibrium with one of the components being retained a considerable chemical dispersion can be observed. In Fig. 4-3 the concentration profiles corresponding to the A $\rightleftarrows$ B system exhibiting $k_1=k_{-1}=0.1\ y^{-1}$, $R_f(A)=1$ and $R_f(B)=2$ are depicted. From a simple distribution coefficient approach it was to be expected that A would be eluted after 100 years, whereas the elution of component B would appear after 200 years. In Fig. 4-4 the elution curves corresponding to the described system are shown, unambiguously demonstrating that the two species are eluted simultaneously at the average time, i.e. 150 years. Qualitatively the same featutures developed in the case of $R_f(A)=2$ and $R_f(B)=1$. It should be noted that the phenomenon here described is not associated with the equality of k_1 and k_{-1}. The <u>average elution time</u> phenomenon is observed as long as the reactions are rapid compared to the residence time of the components in the column.

Systems exhibiting $R_f(A)\neq R_f(B)$ and one of the reactions being significant slower than the other develop 'tailing' and dispersion characteristics analogously to those described in section 4.2. The system exhibiting $k_1=0.1$ $k_{-1}=0.01\ y^{-1}$, $R_f(A)=2$ and $R_f(B)=1$ may serve as an illustrative example (cf. Fig.'s 4-5 and 4-6). It is noted that in the case of equilibria, the dispersion phenomena, due to the chemistry involved, affects both components.

4.5. A $\overset{\rightarrow}{\leftarrow}$ B → C

The chemistry which could be associated with the A $\overset{\rightarrow}{\leftarrow}$ B → C system includes e.g. redox equilibria between the components A and B accompanied by an irreversible transformation (first order or pseudo first order) of the species B. The transformation could be chemical, e.g. inclusion in colloidal material, or microbial, as Pu^{III} $\overset{\rightarrow}{\leftarrow}$ Pu^{IV} → colloidal-Pu.

Hence, the A $\overset{\rightarrow}{\leftarrow}$ B → C system constitutes a superposition of the systems A $\overset{\rightarrow}{\leftarrow}$ B and B → C, which are described in sections 4.4. and 4.2., respectively. Thus, in the case of a rapid equilibrium, or at least a rapid A → B reaction, combined with a relatively rapid B → C reaction, the system can, due to the irreversability of the latter reaction, be treated as the simple irreversible reaction sequence described in section 4.3. On the other hand, in cases of very slow B → C reactions, the system turns out as the simple A $\overset{\rightarrow}{\leftarrow}$ B equilibrium treated in section 4.4. Finally, it is obvious that in cases of very slow A → B reactions the system mimics the "A" system (cf. section 4.1). On this background only the intermediary cases shall be analyzed in the following, the reference case (concentration profiles and elution curves, respectively), i.e. $R_f(A)=R_f(B)=R_f(C)=1$ and $k_1=k_{-1}=k_2=0.1\ y^{-1}$ being elucidated in Fig.'s 5-1 and 5-2.

The influence of possible variation in the retention behaviour is illustrated in two series of figures, in all cases depicted $k_1=k_{-1}=k_2=0.1\ y^{-1}$. The first series comprising Fig.'s 5-3 through 5-5 (concentration profiles) and Fig.'s 5-6 through 5-8 (elution curves) illustrates the effects of an increased retention of A, B, and C, respectively, the initial conditions (i.e. the time t=0) being $[A]=1$, $[B]=[C]=0$ mol m^{-3}. Analogously the second series, comprising Fig.'s 5-9 - 5-11 (concentration profiles) and Fig.'s 5-12 - 5-14 (elution curves) corresponds to the

initial conditions [B]=1, [A]=[C]=0 mol m^{-3}. Obviously the third possiblity, exhibiting the concentration of A and B equal to zero for t=0 and the C concentration different from zero is of no practical interest.

Comparing the illustrations, visualizing the migration behaviour of the components in the A $\rightleftarrows$ B $\rightarrow$ C system with those corresponding to the A $\rightleftarrows$ B system (section 4.4) and the B $\rightarrow$ C system (section 4.2), it appears obvious that the effects unambiguously can be analyzed in terms of superpositions of the two sub-systems, respectively, with regard to 'tailing', dispersion and elution characteristics.

4.6. A $\rightleftarrows$ B $\rightleftarrows$ C

The double equilibrium system A $\rightleftarrows$ B $\rightleftarrows$ C represents reactions like redox equilibria involving three separate oxidation states, or a redox equilibrium A $\rightleftarrows$ B, in which component B by a pseudo first order reaction, e.g. complex formation, reversibly is converted into C, as $Tc^{VII}O_4^-$ $\rightleftarrows$ Tc^{IV}(Citric Acid).

Since the system consists of two superposed equilibria, it is obvious that for certain values of k_1, k_{-1}, k_2, and k_{-2} the system will behave as the single equilibrium system A $\rightleftarrows$ B as described in section 4.4. This will be the case when k_{-1} (B $\rightarrow$ A) or k_2 (B $\rightarrow$ C) are very low. In the case of a slow C $\rightarrow$ B reaction the system can be rationalized as the above described A $\rightleftarrows$ B $\rightarrow$ C system (cf. section 4.5.).

The reference case, i.e. $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}, $R_f(A)=R_f(B)=R_f(C)=1$ is illustrated in Fig. 6-1 (concentration profiles) and Fig. 6-2 (elution curves), the initial conditions being [A]=1, [B]=[C]=0. An almost identical picture is developed for the initial conditions being [A]=[C]=0, [B]=1.

The effect of changes in the retention behaviour on the migration behaviour of A, B, and C, respectively, is visualized, for the initial conditions being [A]=1, [B]=[C]=0, in the series of figures Fig.'s 6-3 through 6-5 (concentration profiles) and Fig.'s 6-6 through 6-8 (elution curves) for A, B, and C being retained, respectively (all rate constant are set equal to 0.1 y^{-1}). The more predominant feature unambiguously is the 'tailing' phenomena and hence, the dispersion.

In Fig.'s 6-9 and 6-10 the concentration profiles and the elution curves for the case $R_f(A)=1$, $R_f(B)=2$, $R_f(C)=3$, all rate constants equal to 0.2 y^{-1}, and initially [A]=1, [B]=[C]=0 are depicted. As was the case for the simple A $\rightleftarrows$ B equilibrium system, the elution curves may at first sight seem somewhat surprising. From the simple R_f-approach elution times at 100, 200, and 300 years, respectively, would be expected for A, B, and C. However, an average elution time at ca. 200 years is observed for all three components.

A similar set of calculations using [A]=[C]=0, [B]=1 as initial conditions developed an analogous picture to the above described.

The equilibrium constants, i.e. the rate constants have a significant influence on the migration behaviour. A series of figures, to be compared with the above described, for the systems exhibiting $k_1=k_{-1}=0.1$ y^{-1} and $k_2=k_{-2}=0.001$ y^{-1} is given in Fig.'s 6-11 to 6-13 (concentration profiles; compare to Fig.' 6-3 to 6-5) and Fig.'s 6-14 to 6-16 (elution curves; compare to Fig.' 6-6 to 6-8).

A general feature observed is an increased dispersion. Not unexpected are the elution curves for the case $R_f(A)=2$, $R_f(B)=R_f(C)=1$ (Fig. 6-14) and $R_f(A)=R_f(C)=1$ and $R_f(B)=2$ (Fig. 6-15) nearly identical, whereas the third possibility, i.e. $R_f(A)=R_f(B)=1$, $R_f(C)=2$ revealed a pronounced dispersion of C relative to A and B (Fig. 6-16).

Changing the initial conditions to [A]=[C]=0, [B]=1 mol m^{-3} a nearly identical picture developed in the cases where $R_f(B)$ and $R_f(C)$ were set equal to two (cf. Fig.'s 6-12, 6-15, and Fig.'s 6-13 and 6-16, respectively). In the case of $R_f(A)=2$, $R_f(B)=R_f(C)=1$ a picture somewhat different from the above described (cf. Fig. 6-11 and Fig. 6-14) appeared, as illustrated in Fig.'s 6-17 and 6-18, respectively. Especially component C apparently is affected.

Finally, the system exhibiting two slow equilibria shall be analyzed. Applying [A]=1, [B]=[C]=0 as initial condition almost no C is formed, i.e. the system turns into the simple single equilibrium system (cf. section 4.4). Hence, in this connection only [B]=1, [A]=[C]=0 as initial condition is of interest, the rate constants are all set equal to 0.001 y^{-1}. Retention of A, relative to B and C afforded, apart from significant dispersion of component A also the expected delayed retention of A relative to B and C (Fig.'s 6-19 and 6-20). Owing to the 'symmetry' of the system the exact same picture was seen in the case of retained C, i.e. dispersion and delayed elution of component C. However, in the case of retardation of B ($R_f(B)=2$, $R_f(A)=R_f(C)=1$) a somewhat different picture develops (Fig.'s 6-21 and 6-22). Component B is in this case found to be significantly delayed simultaneously with pronounced dispersion of components A and C.

4.7. A + X → B

The irreversible reaction between a component A with X, the latter being supplied in large excess, to give B is a typical pseudo first order reaction.

In the present context we use this type of reaction to elucidate the effect of a sudden change in ground water composition resulting in mobilization of A, B denoting the 'mobile form of A'. Hence, at

t=0 A is assumed to be fixed in part of the column (which in practice was done by putting $R_f(A)=100$), here $0<x<75$ m. B and X are assumed to move without retention. X, which for $t>0$ continuously flows into the column may be intrusion of complexing agents in which case B corresponds to complexed A (i.e. B ≡ AX: Co + EDTA → Co(EDTA)), or simply a breakthrough of e.g. highly saline ground water mobilizing A. In the latter case B ≡ A, as e.g. Sr^{2+} bound by ion exchange to clay material.

In Fig.'s 7-1 and 7-2 the concentration profiles are shown corresponding to rate constants $k_1=1$ and 10 $M^{-1}\ y^{-1}$, respectively. It is seen that in the case of the slower reaction only part of the component A is mobilized within the time frame studied, whereas the rapid reaction results in an almost quantitative mobilization of A. The corresponding elution curves are shown in Fig.'s 7-3 and 7-4, the very rapid concentration increase of B at the break-through point being noted.

4.8. A + B ⇕ C

The reversible second order/first order system elucidates the reaction between the species A and B, in comparable concentrations leading to C, the reverse process being of first order. The system could illustrate complex formation, A (or B) and C being the ligand and the complexed species, respectively, e.g. Eu + Hunic Acid ⇕ Eu(Humic Acid).

A priori two sets of initial concentration conditions can be studied: a) $[A]=[B]=1$, $[C]=0$, or b) $[A]=[B]=0$, $[C]=1$. In the latter case, combined with a slow second order reaction, either due to a low second order rate constant and/or low concentrations of A and B, which will not be unusual in geochemical systems, the system turns out as a simple first order reaction C → A + B. (cf.

The simple reference case (valid for both initial conditions), i.e. $R_f(A)=R_f(B)=R_f(C)=1$, $k_1=0.1\ M^{-1}\ y^{-1}$, and $k_{-1}=0.1\ y^{-1}$ is illustrated in Fig.'s 8-1 and 8-2 depicting the concentration profiles and the elution curves, respectively.

Studying the effect of retention it is necessary strongly to distinquish between the cases where C is retained and those where A and/or B are retained.
Retention of C, relative to A and B affords, not unexpectedly, a pronounced dispersion of component C, although the three components, in cases of rapid equilibria will be eluted simultaneously. In Fig.'s 8-3 and 8-4 the concentration profiles and elution curves for the system exhibiting $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $k_1=0.1\ M^{-1}\ y^{-1}$ $k_{-1}=0.1\ y^{-1}$ (initial conditions a) being applied), are shown. The alternative input concentrations (initial conditions b)) revealed an almost identical picture.

Lowering the first order rate constant by a factor of 100 resulted in dispersion effects depending of the initial conditions as visualized in Fig.'s 8-5 and 8-6 (concentration profiles) and Fig.'s 8-7 and 8-8 (elution curves).

On the other hand, if B (or A) is retained the problem arises that C can be formed only if A <u>and</u> B are present at the same position in the column at a given time. Thus, in case of the rapid equilibrium (Fig.' 8-9 and 8-10) the disappearence of C is easily visualized. Lowering the first order rate constant a certain portion of C survives, due to its decreased disppearence rate, as illustrated in Fig.'s 8-11 and 8-12, C being eluted simultaneously with A. Similar effects are seen in cases where $R_f(A)=1$, $R_f(B)=R_f(C)=2$, (cf. Fig.'s 8-13 and 8-14), however, C being eluted like B.

Finally, the effect of $R_f(A)=R_f(B)=2$, $R_f(C)=1$ shall be illustrated. Not surprisingly significant dispersion of component C is noted,

Not surprisingly significant dispersion of component C is noted, all three species, however, being eluted simultaneously, in case of a rapid equilibrium (Fig.'s 8-15 and 8-16), a feature which is changed by lowering the first order reaction rate (cf. Fig.'s 8-17 and 8-18).

The above described examples in all cases refer to the initial conditions of type a). The alternative conditions (type b)), developed in cases of rapid equilibria nearly identical pictures, whereas lowering the first order reaction rate causes significant changes in the dispersion/elution characteristics of the three components, as visualized in Fig.'s 8-19 and 8-20 (concentration profiles) and Fig.'s 8-21 and 8-22 (elution curves). Hence, retention of B and C caused dispersion of A, whereas retention of A and B resulted in significant increased dispersion of A and B.

4.9. $A + B \rightleftarrows C + D$

The scond order equilibrium system may be associated with ligand exchange reaction, af Ca(Humic Acid) + EDTA $\rightleftarrows$ Ca(EDTA) + Humic Acid, which has been suggested to play an important role in the migration of radionuclides (Carlsen, 1985). The above mentioned features for the second order reaction also apply to the $A+B \rightleftarrows C+D$ system. Only one set of initial concentration conditions, namely $[A]=[B]=1$, $[C]=[D]=0$, has been considered, the reference case, i.e. no retention, has been visualized in Fig.'s 9-1 and 9-2 for $k_1=k_{-1}=0.1\ M^{-1}\ y^{-1}$.

The influence of retention, of one or more of the components, is elucidated through the Fig.'s 9-3 through 9-6 (concentration profiles) and Fig.'s 9-7 through 9-10 (elution curves) for retention

of B, B and D, C and D, and B, C and D, respectively. In all cases the immediately expected behaviour can be observed. Variations in the mutual rate constants within up to 1 order of magnitude do only change the mutual concentration ratios between the four components, however, maintaining the overall picture. Only in the case of a relatively slow equilibrium ($k_1=k_{-1}=0.01$ M^{-1} y^{-1}) with C and D retained relative to A and B a pronounced dispersion of the former two components could be noted (cf. Fig.'s 9-11 and 9-12).

5. CONCLUSION

The study unambiguously discloses the importance of the 'chemistry' in predicting the migration behaviour of pollutants, e.g. radionuclides in the terrestrial environment.

The above analyzed reaction systems lead to the conclusion that the interplay between the retention characteristics for the single components and the mutual interconversion rates controls the migration behaviour, i.e. residence times and dispersion characteristics. The term 'chemical dispersion' is emphasized for these kinetically induced phenmomena.

The study suggests that besides estimation of retention characteristics for radionuclides, their possible involvment in chemical and physico-chemical reactions, as complex formation and redox equilibria, should be elucidated, in order to obtain kinetic informations. It is emphasized in this connection that the interaction between organically complexed radionuclides and geologic media need to be studied in detail, an area of research which unfortunately hitherto has been neglected.

Finally the study reveals that prediction of the influence of chemistry can be made based on the knowledge of relatively few fundamental reaction types, when the actual kinetics is known.

6. REFERENCES

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Carlsen, L, Radionuclide - Soil organic matter interactions, Eur. Appl.Res.Rept. - Nucl.Sci.Technol, in press

Nielsen, O.J., Carlsen, L, and Bo, P. (1985), COLUMN2 - A computer program for simulation of migration, in press as EUR 10120/Risø-R514

7. FIGURES

In the following 120 pages all figures are collected in sections corresponding to the single sections of text (cf. index page).

FIGURES FOR SECTION 4.1

A

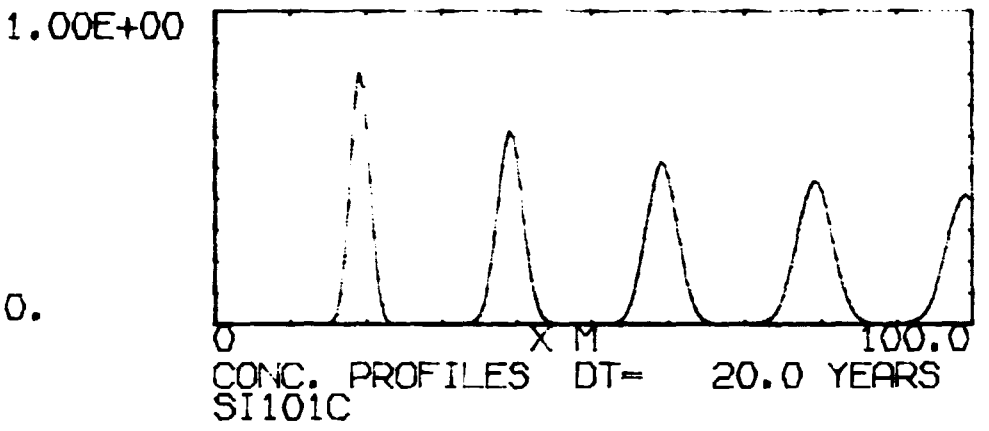

Figure 1-1. $R_f(A)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}.

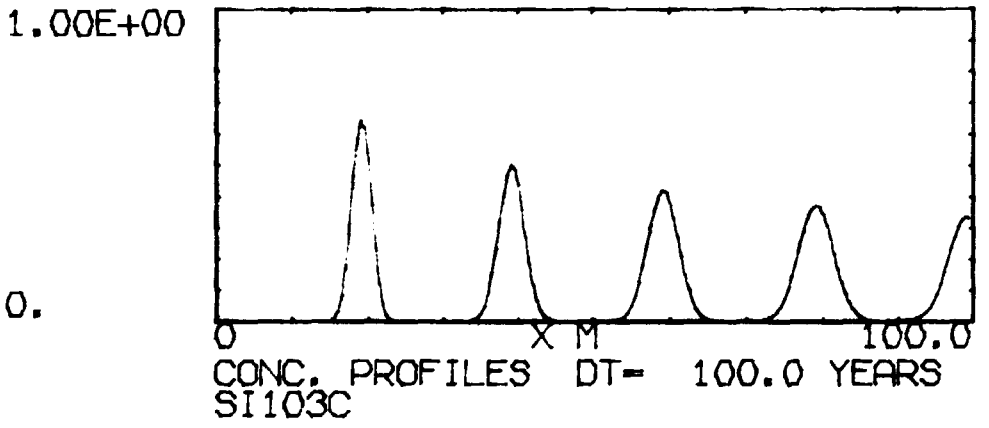

Figure 1-2. $R_f(A)=5$, V=1 m y^{-1}, D=0.03 m y^{-2}.

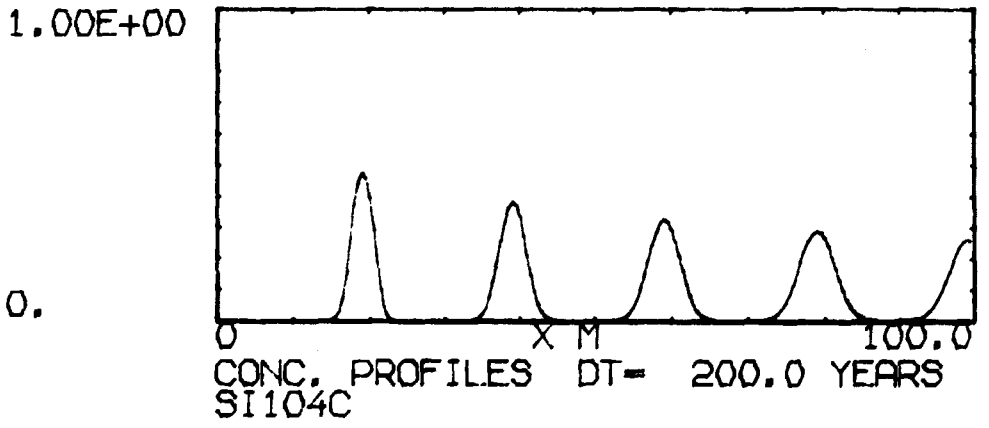

Figure 1-3. $R_f(A)=10$, V=1 m y^{-1}, D=0.03 m y^{-2}.

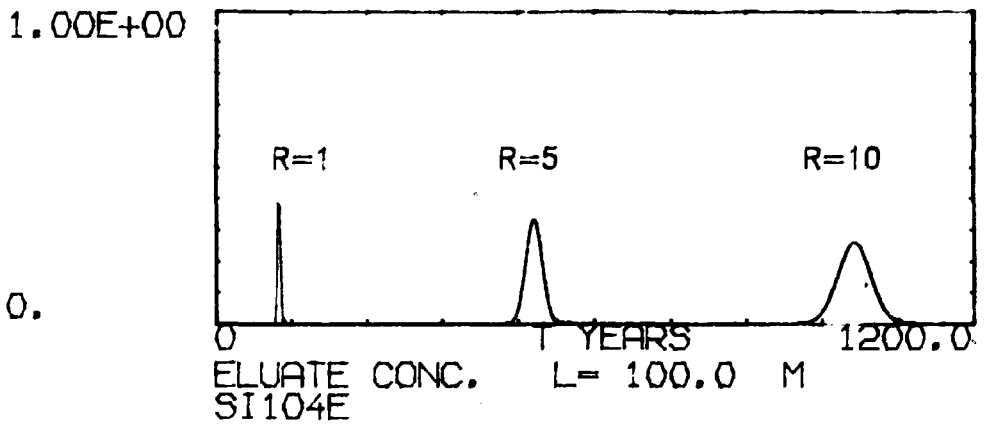

Figure 1-4. $R_f(A)=1,5,10$, V=1 m y^{-1}, D=0.03 m y^{-2}.

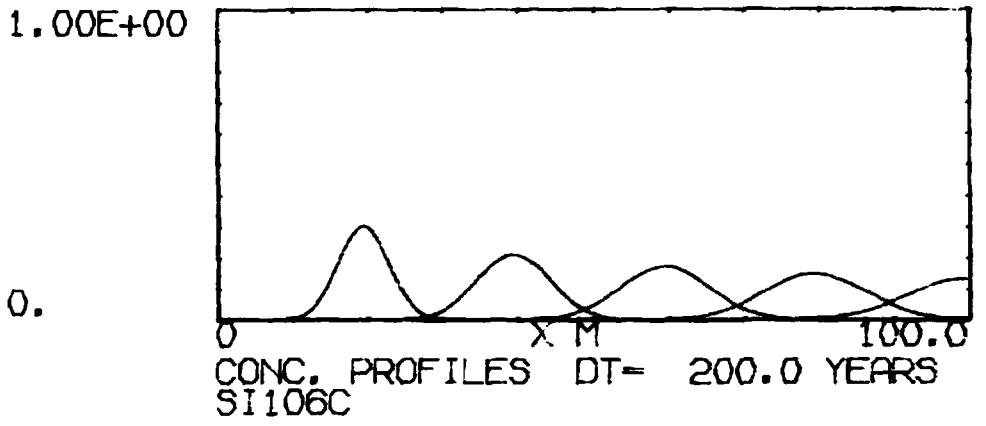

Figure 1-5. $R_f(A)=1$, V=0.1 m y^{-1}, D=0.03 m y^{-2}.

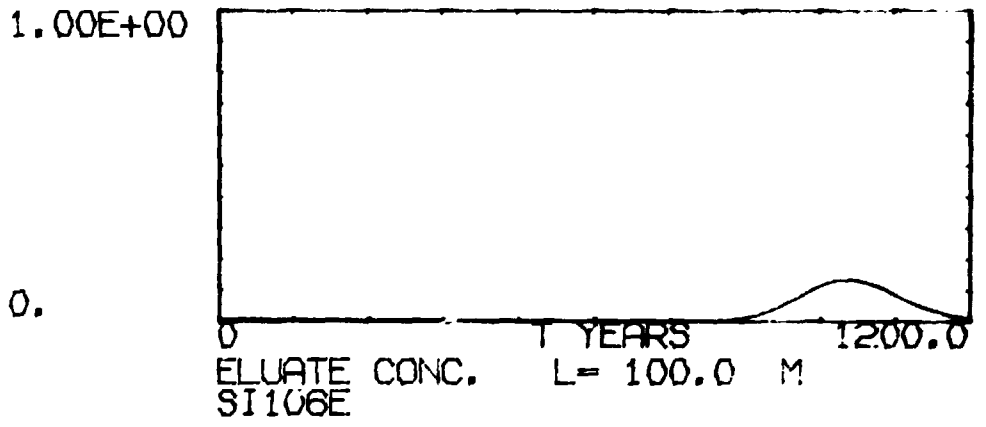

Figure 1-6. $R_f(A)=1$, V=0.1 m y^{-1}, D=0.03 m y^{-2}.

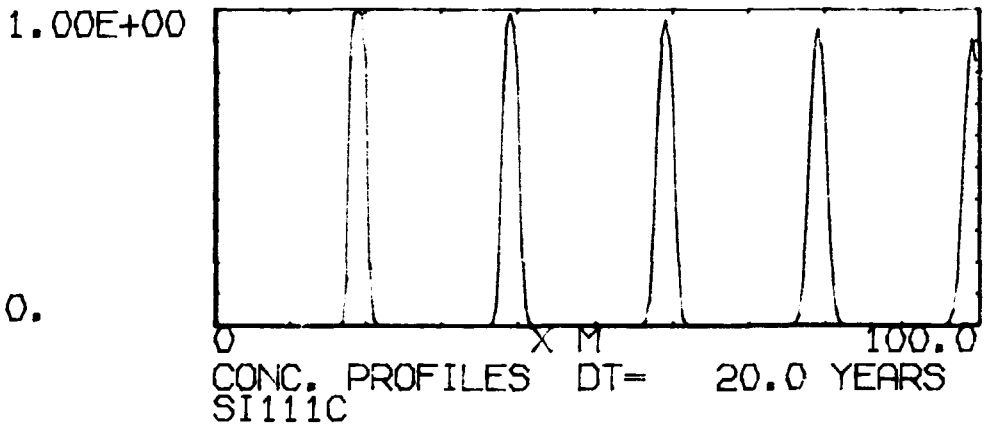

Figure 1-7. $R_f(A)=1$, V=1 m y^{-1}, D=0.003 m y^{-2}.

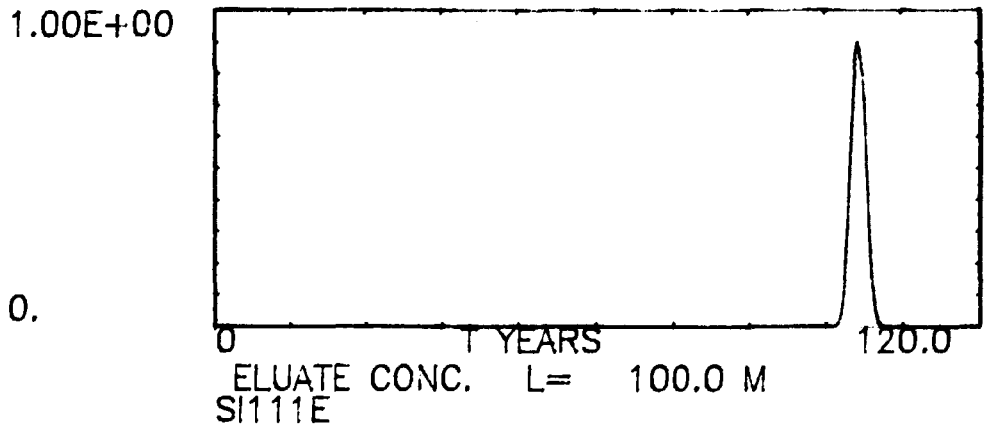

Figure 1-8. $R_f(A)=1$, V=1 m y^{-1}, D=0.003 m y^{-2}.

FIGURES FOR SECTION 4.2

A→B

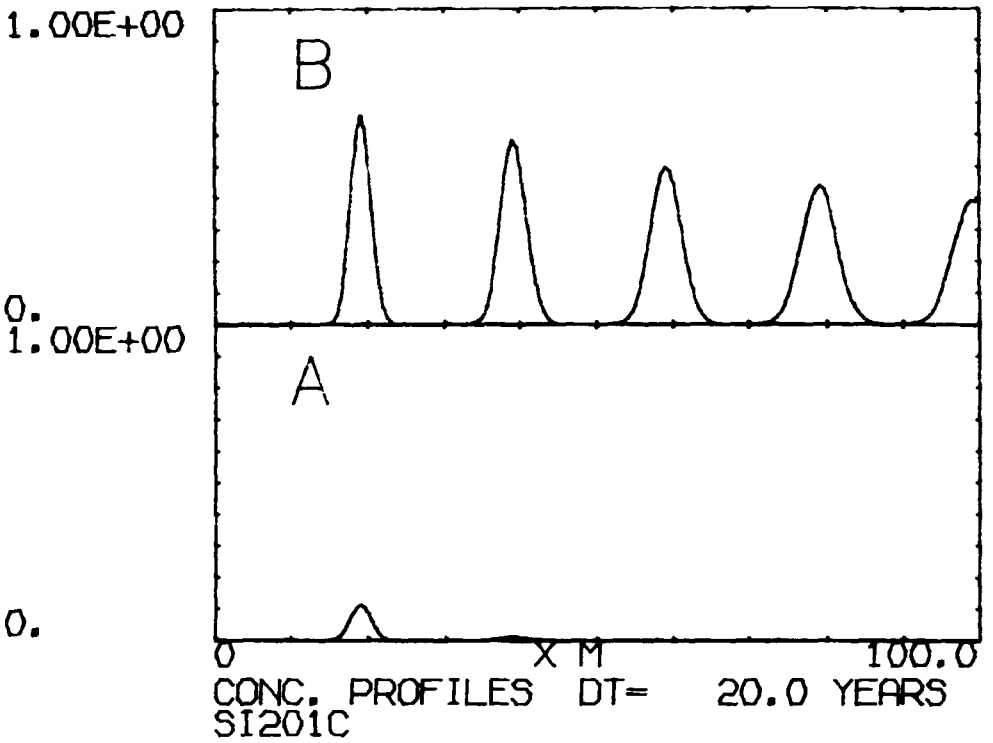

Figure 2-1. $R_f(A)=R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1$ y^{-1}.

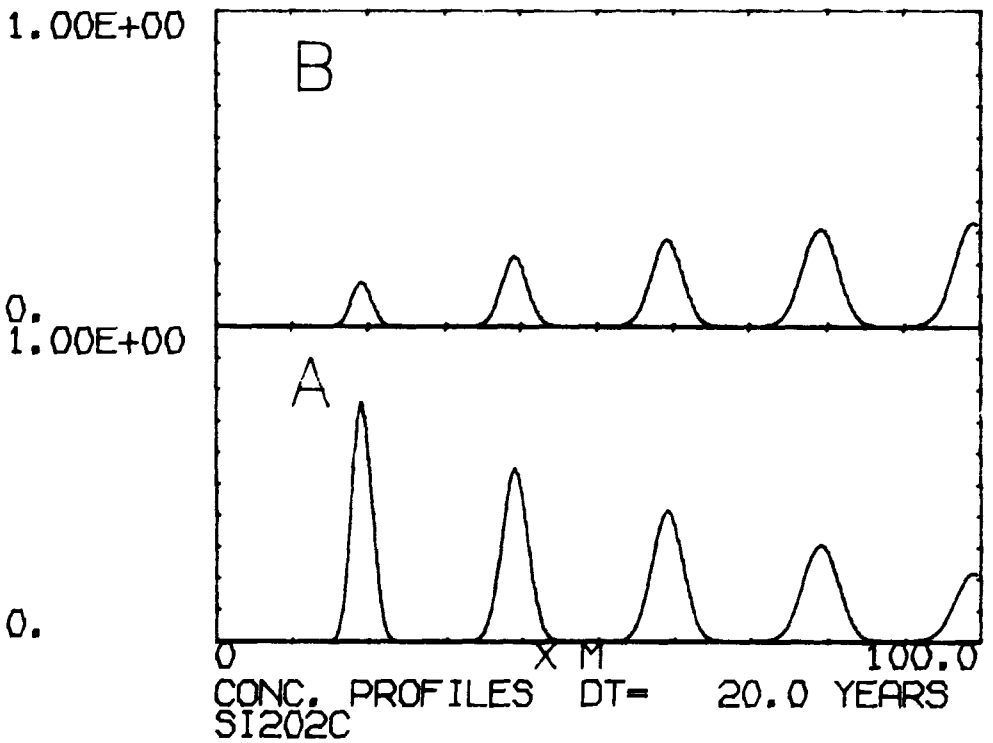

Figure 2-2. $R_f(A)=R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.01$ y^{-1}.

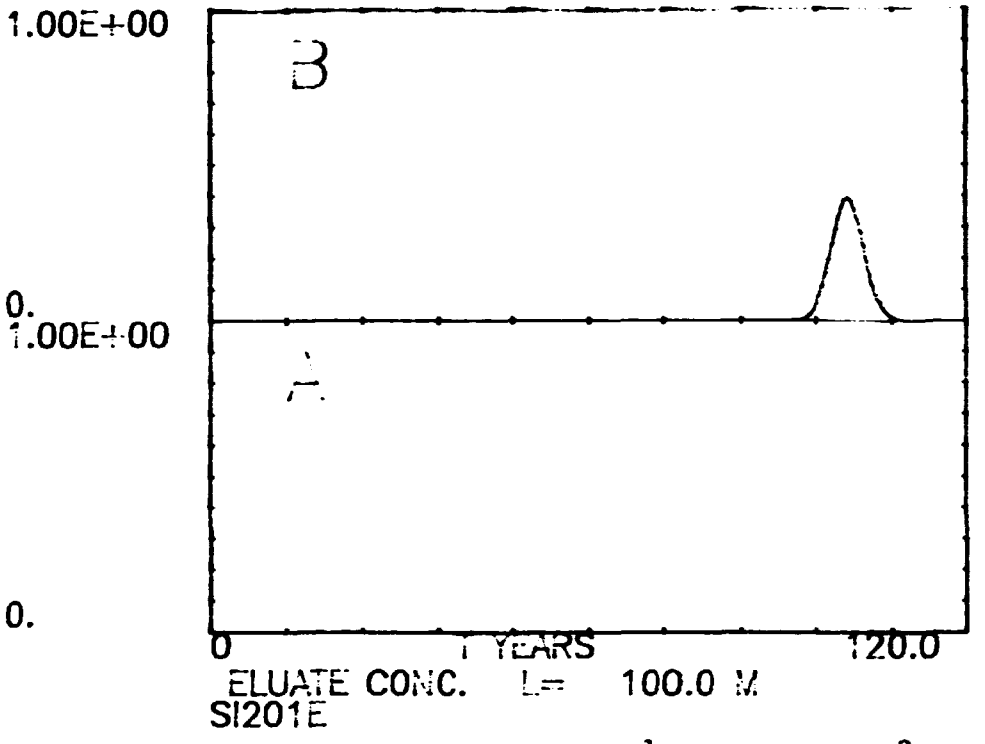

Figure 2-3. $R_f(A)=R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, k_1=o.1 y^{-1}.

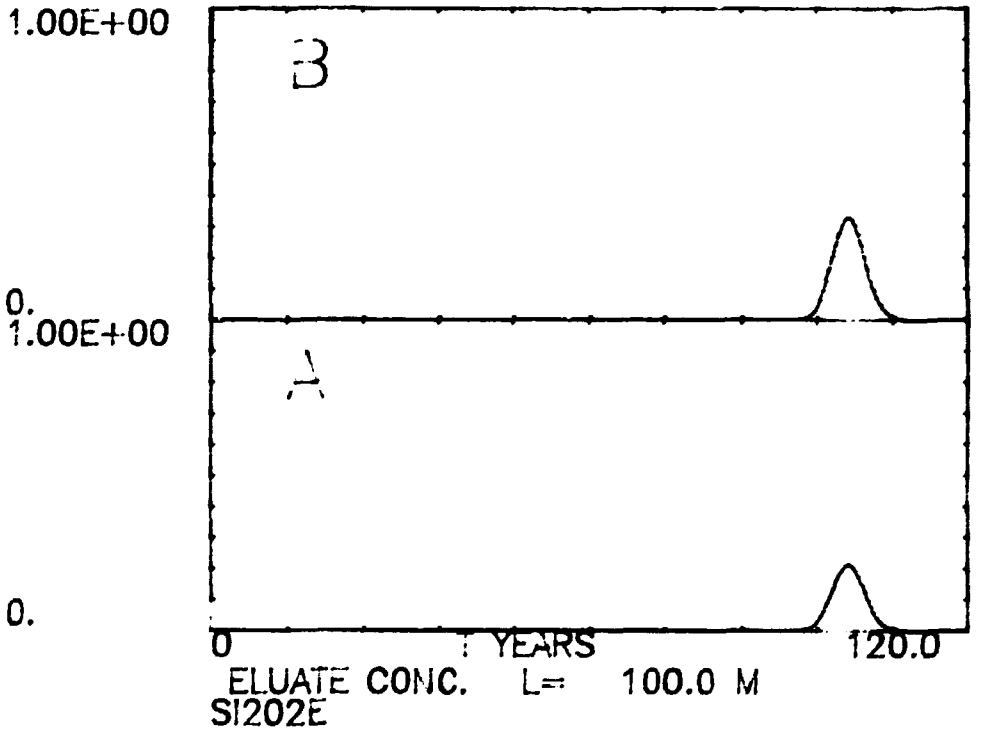

Figure 2-4. $R_f(A)=R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, k_1=0.01 y^{-1}.

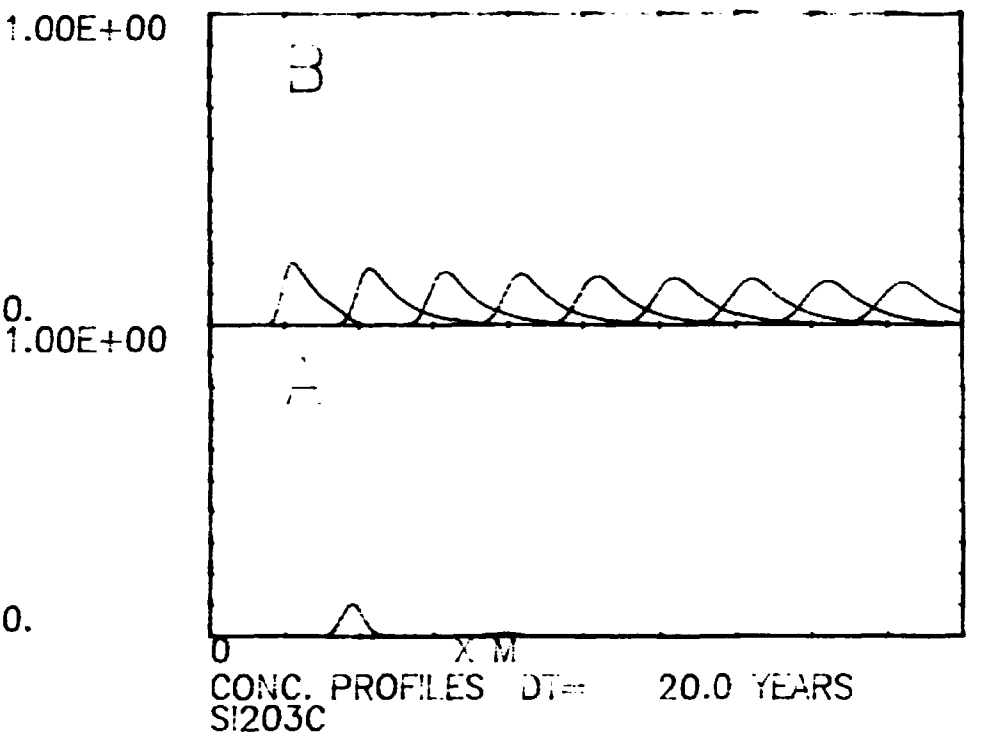

Figure 2-5. $R_f(A)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ y^{-1}.

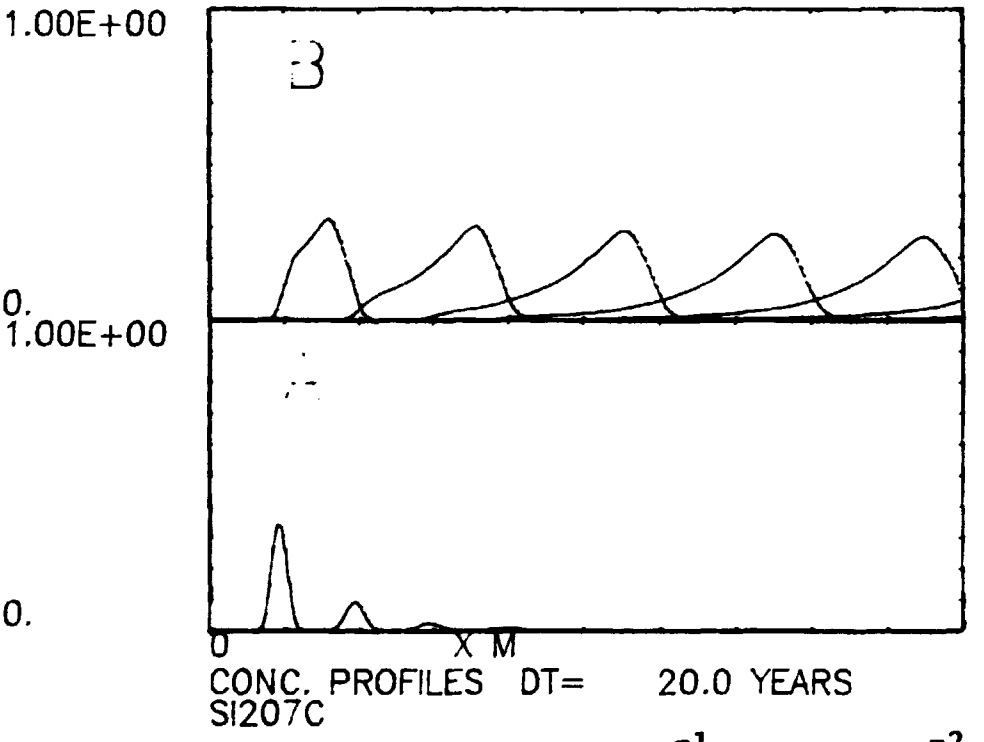

Figure 2-6. $R_f(A)=2$, $R_f(B)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ y^{-1}.

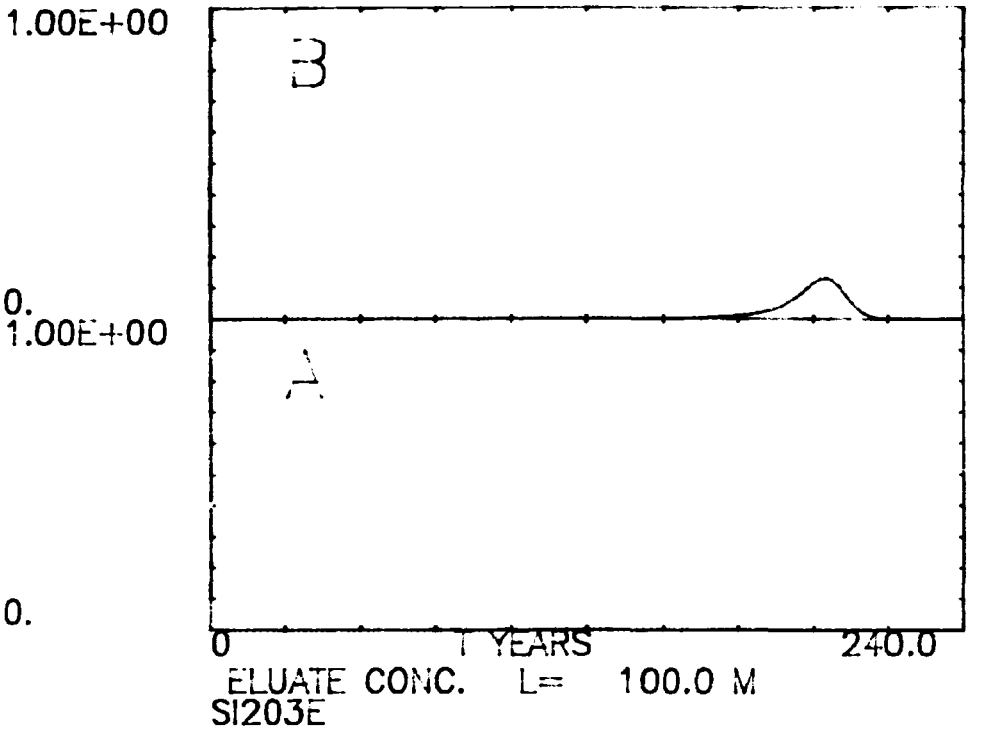

Figure 2-7. $R_f(A)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ y^{-1}.

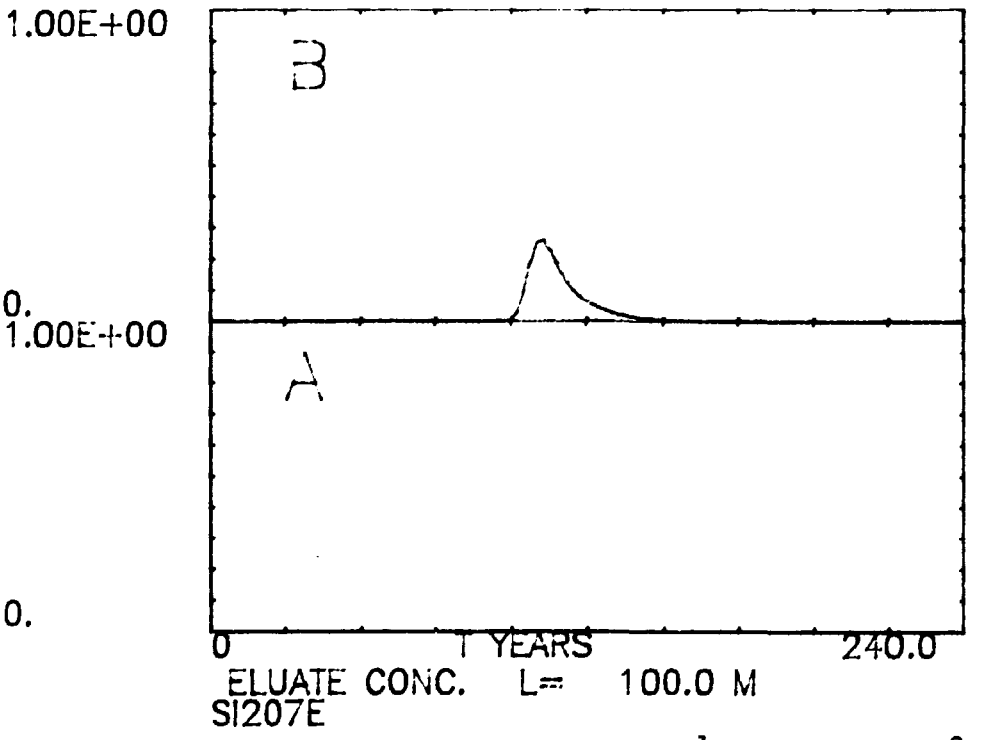

Figure 2-8. $R_f(A)=2$, $R_f(B)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ y^{-1}.

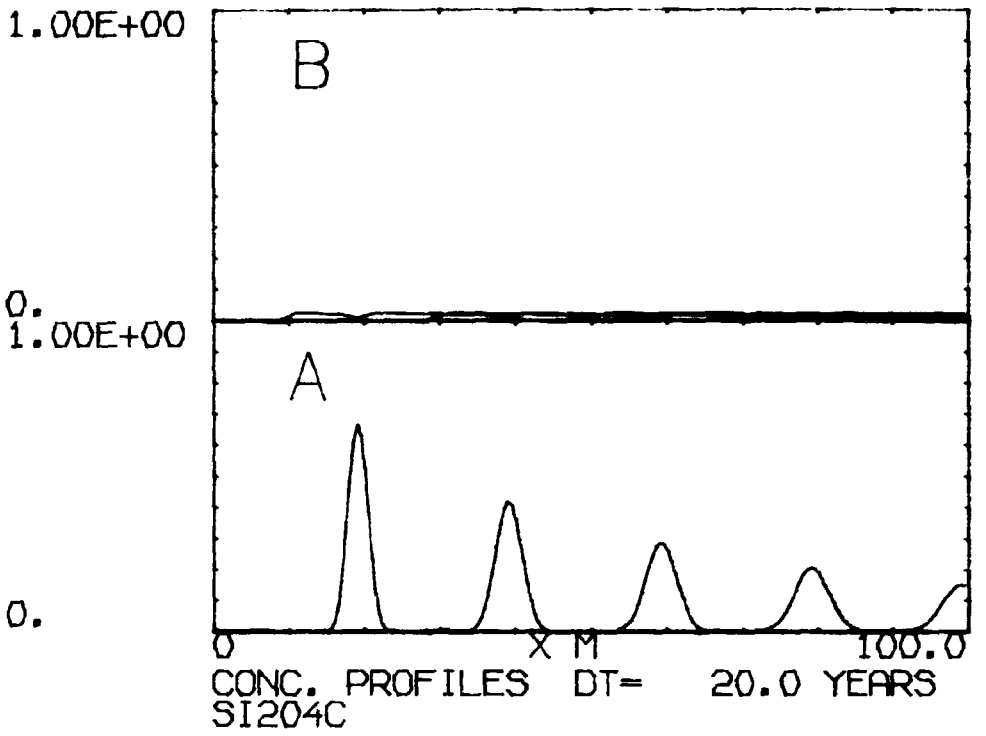

Figure 2-9. $R_f(A)=1$, $R_f(B)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.01$ y^{-1}.

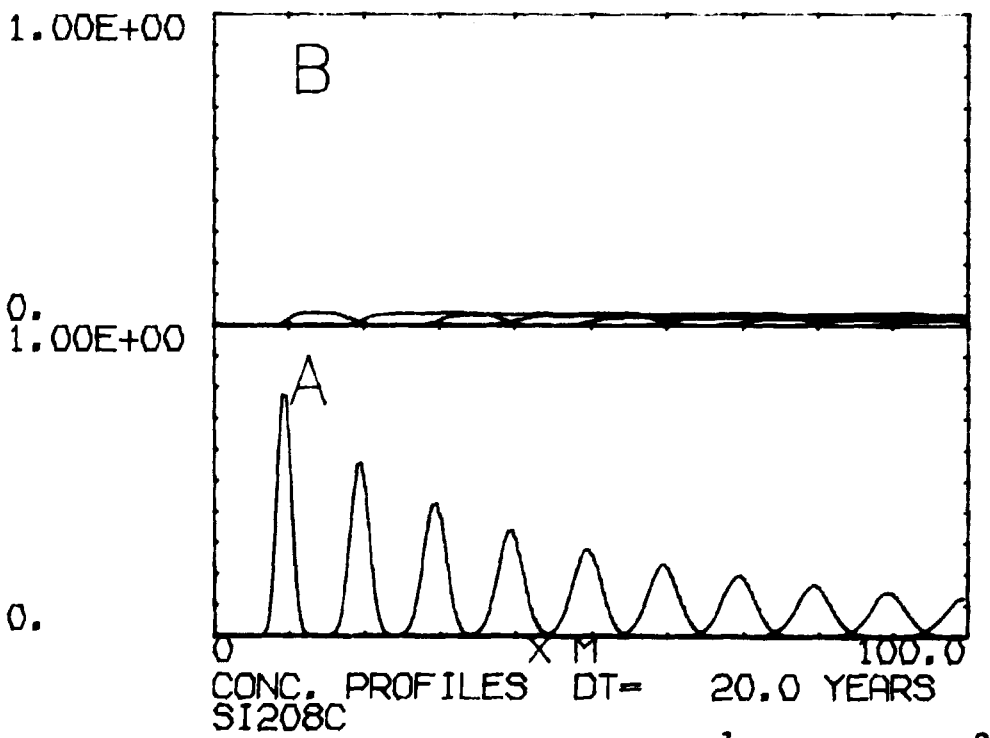

Figure 2-10. $R_f(A)=2$, $R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.01$ y^{-1}.

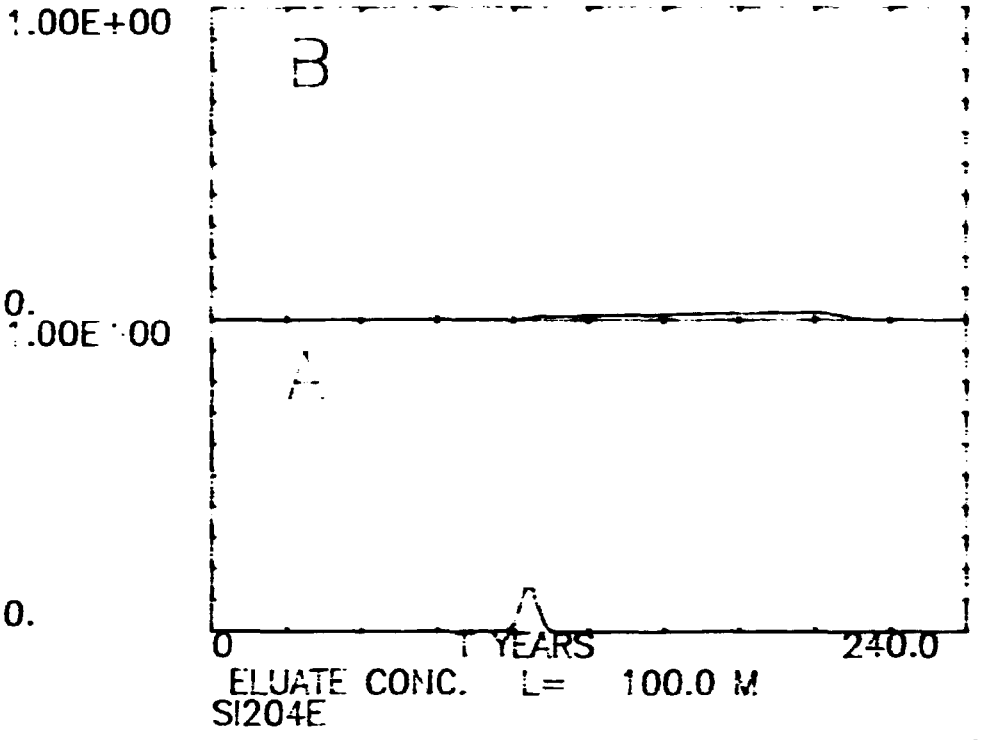

Figure 2-11. $R_f(A)=1$, $R_f(B)=2$, $V=1\ m\ y^{-1}$, $D=0.03\ m\ y^{-2}$, $k_1=0.01\ y^{-1}$.

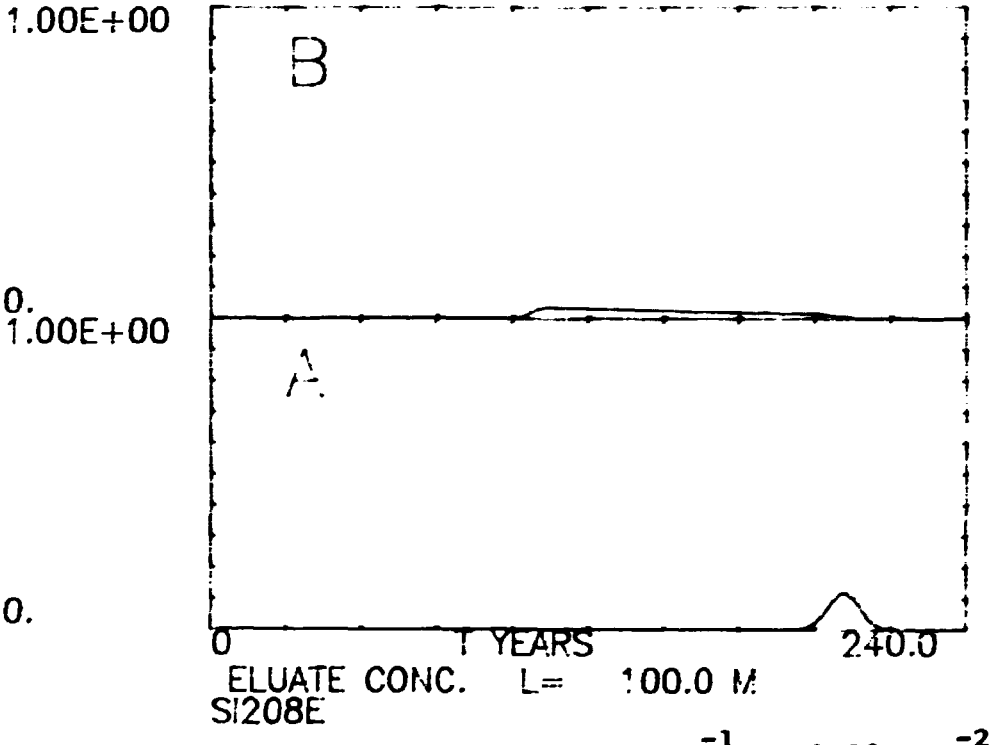

Figure 2-12. $R_f(A)=2$, $R_f(B)=1$, $V=1\ m\ y^{-1}$, $D=0.03\ m\ y^{-2}$, $k_1=0.01\ y^{-1}$.

FIGURES FOR SECTION 4.3

A→B→C

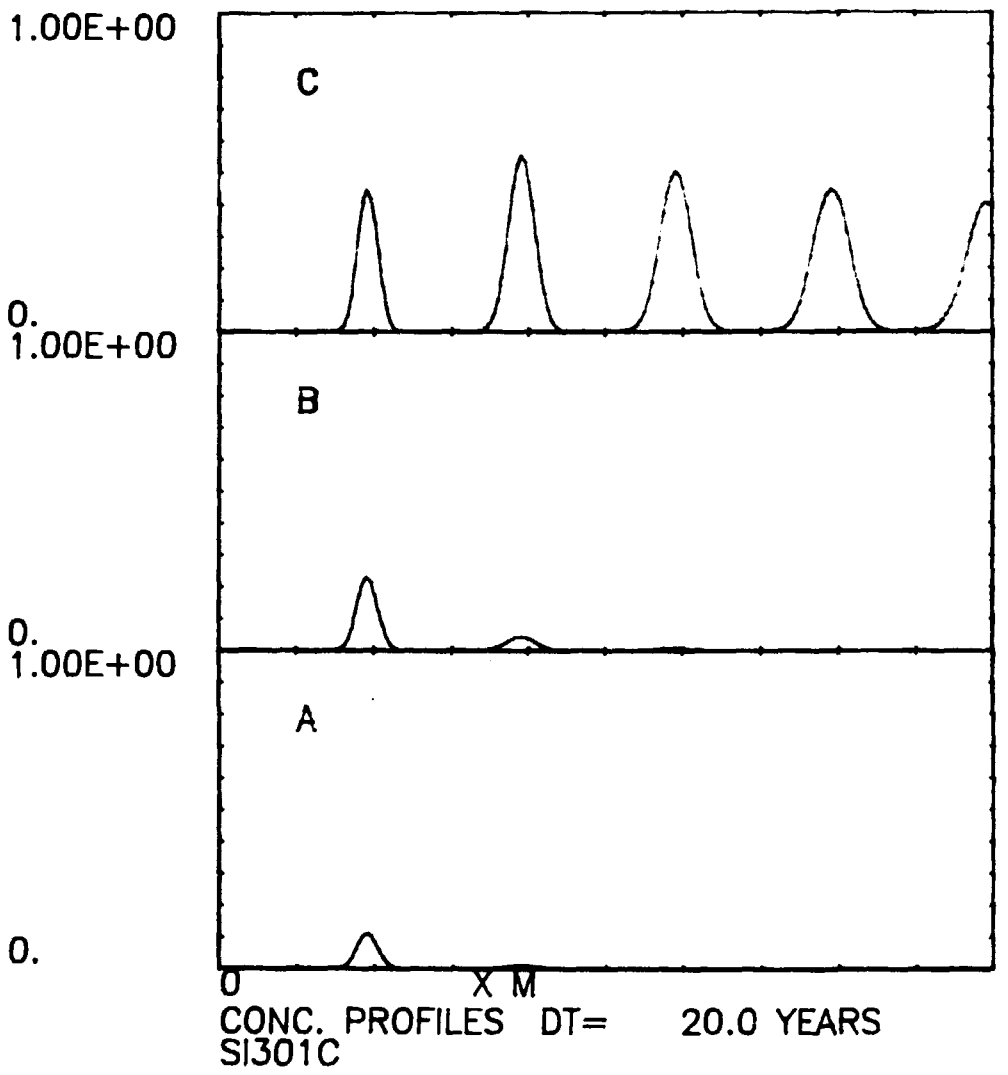

Figure 3-1. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_2=0.1$ y^{-1}.

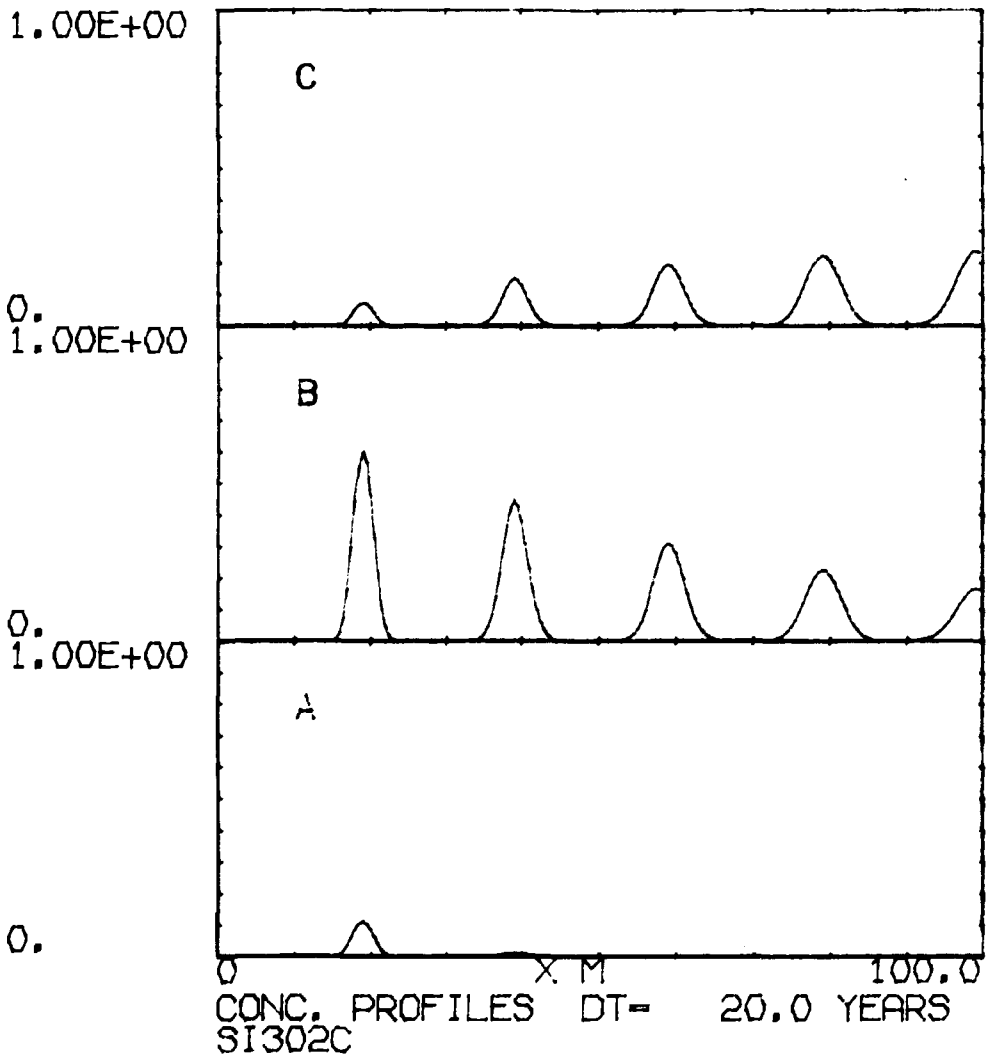

Figure 3-2. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1\ y^{-1}$, $k_2=0.01\ y^{-1}$.

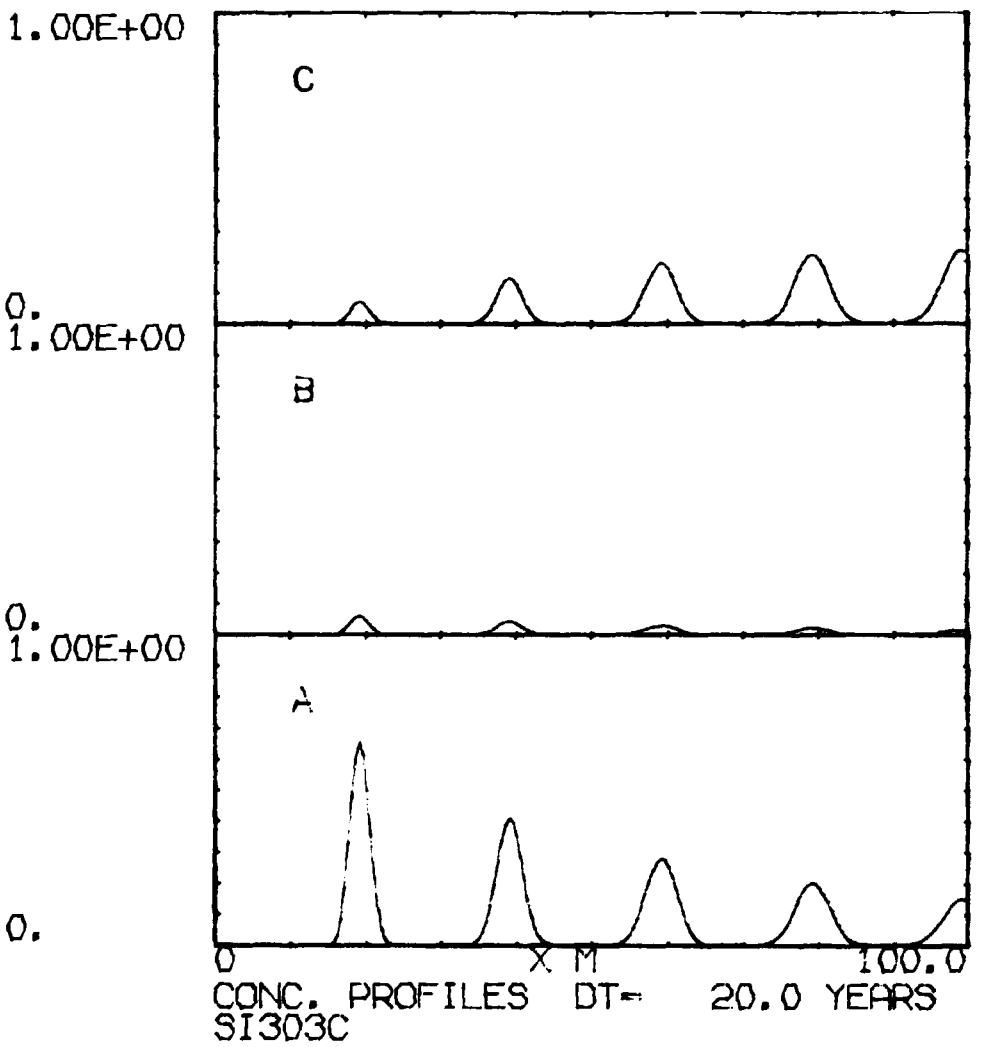

Figure 3-3. $R_f(A)=R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.01$ y^{-1}, $k_2=0.1$ y^{-1}.

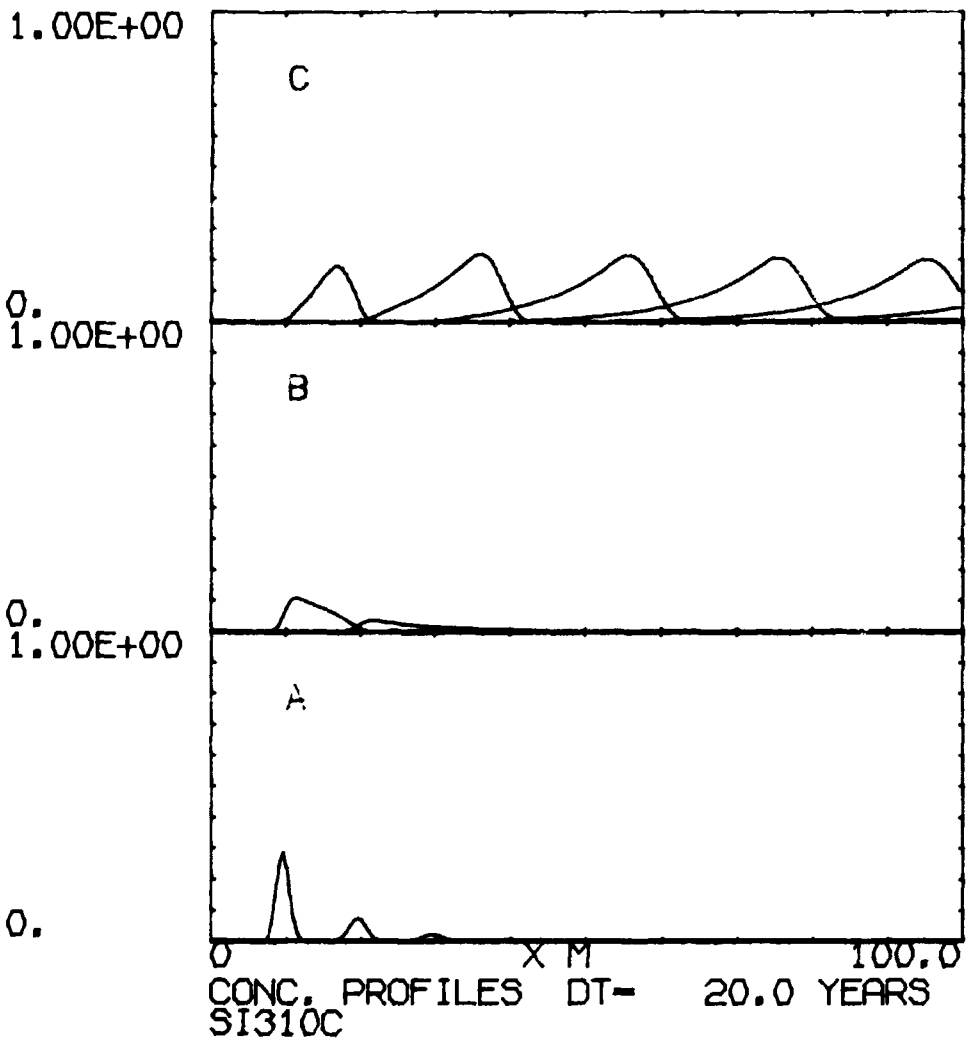

Figure 3-4. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_2=0.1$ y^{-1}.

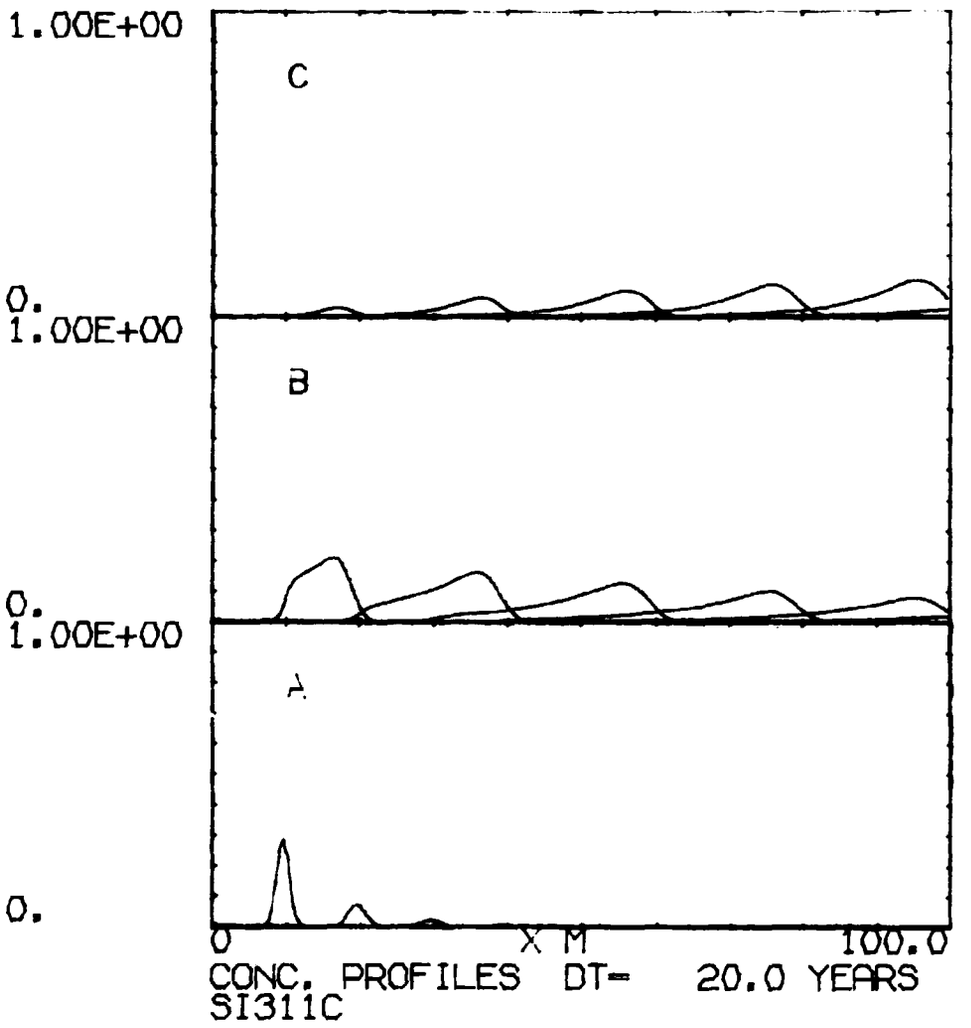

Figure 3-5. $R_f(A)=2$, $R_f(B)=R_f(C)$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ y^{-1}, $k_2=0.01$ y^{-1}.

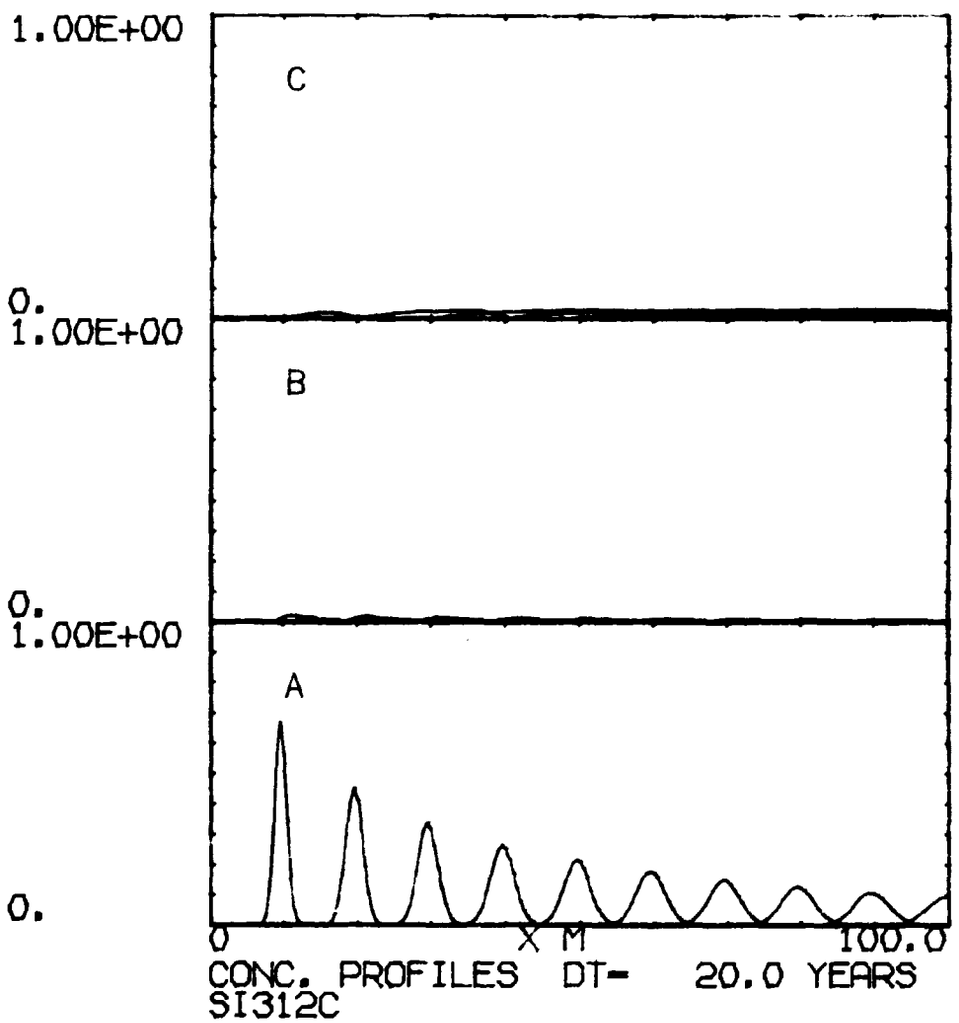

Figure 3-6. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, k_1=0.01 y^{-1}, k_2=0.1 y^{-1}.

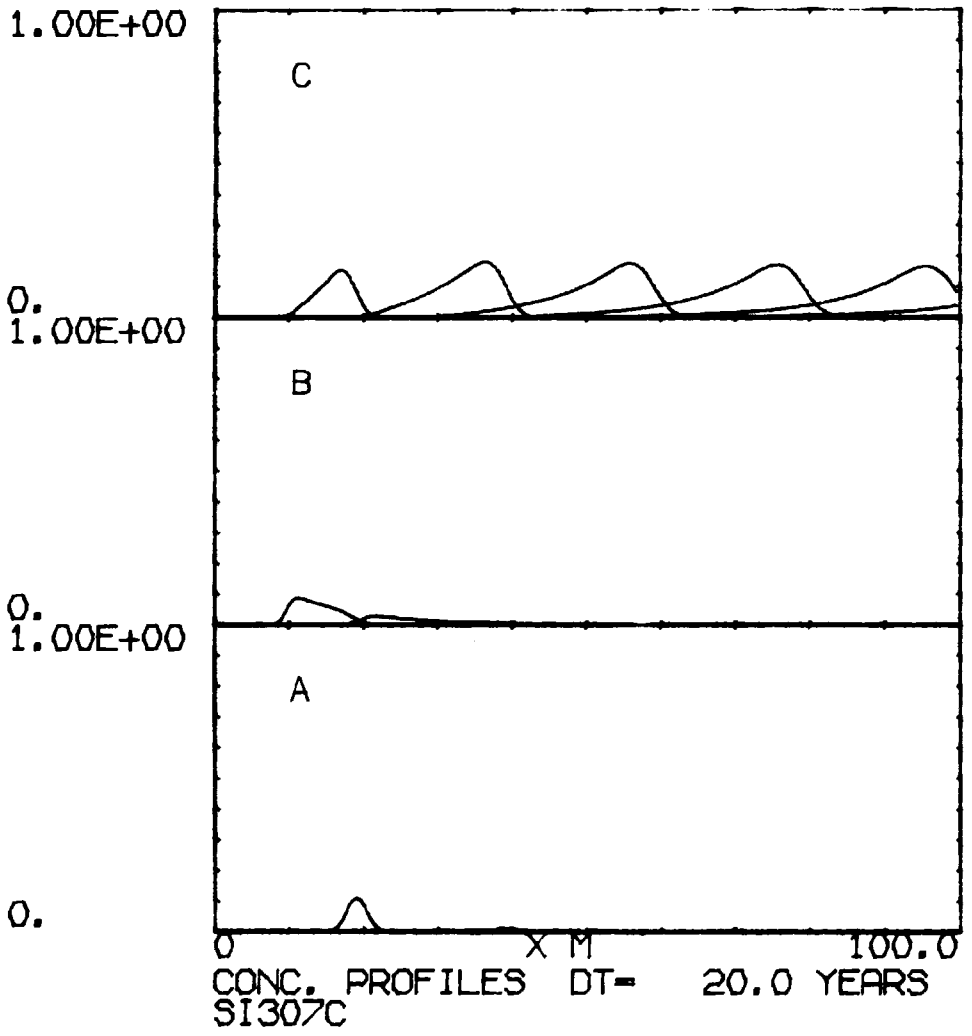

Figure 3-7. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_2=0.1$ y^{-1}.

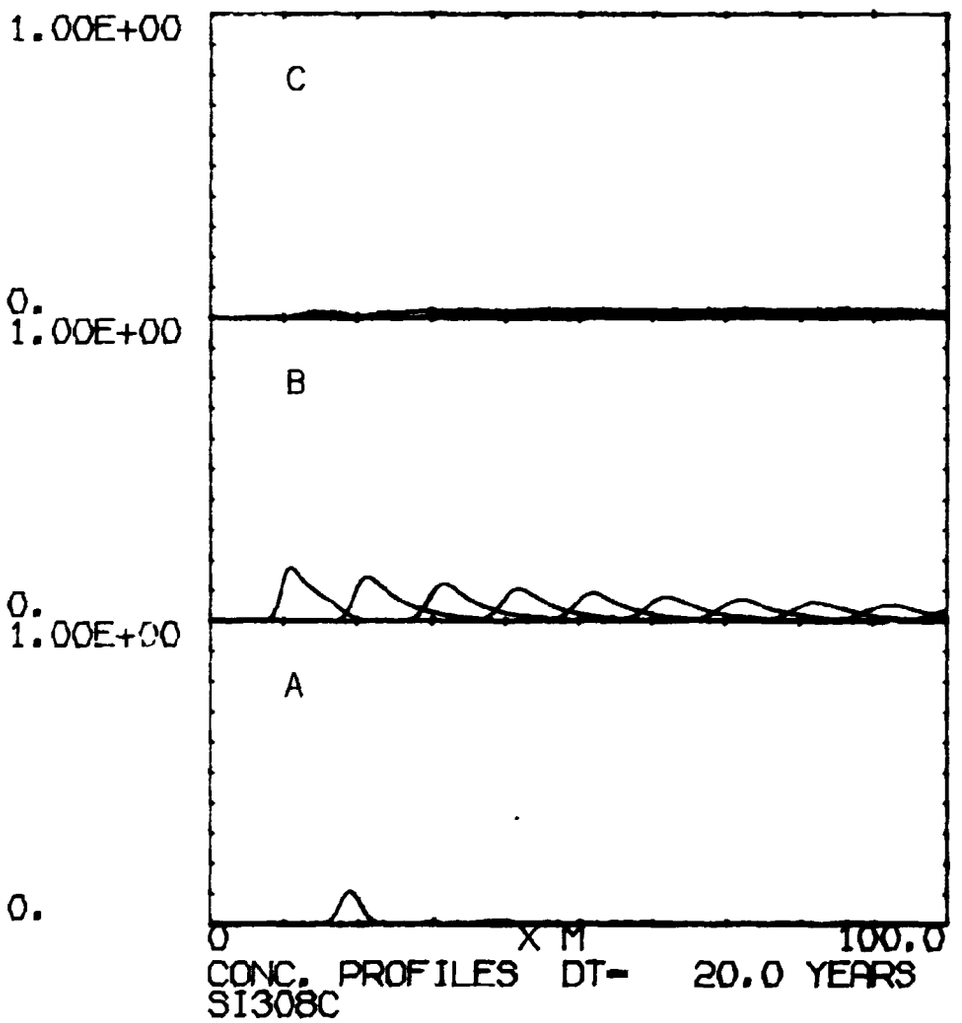

Figure 3-8. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ y^{-1}, $k_2=0.01$ y^{-1}.

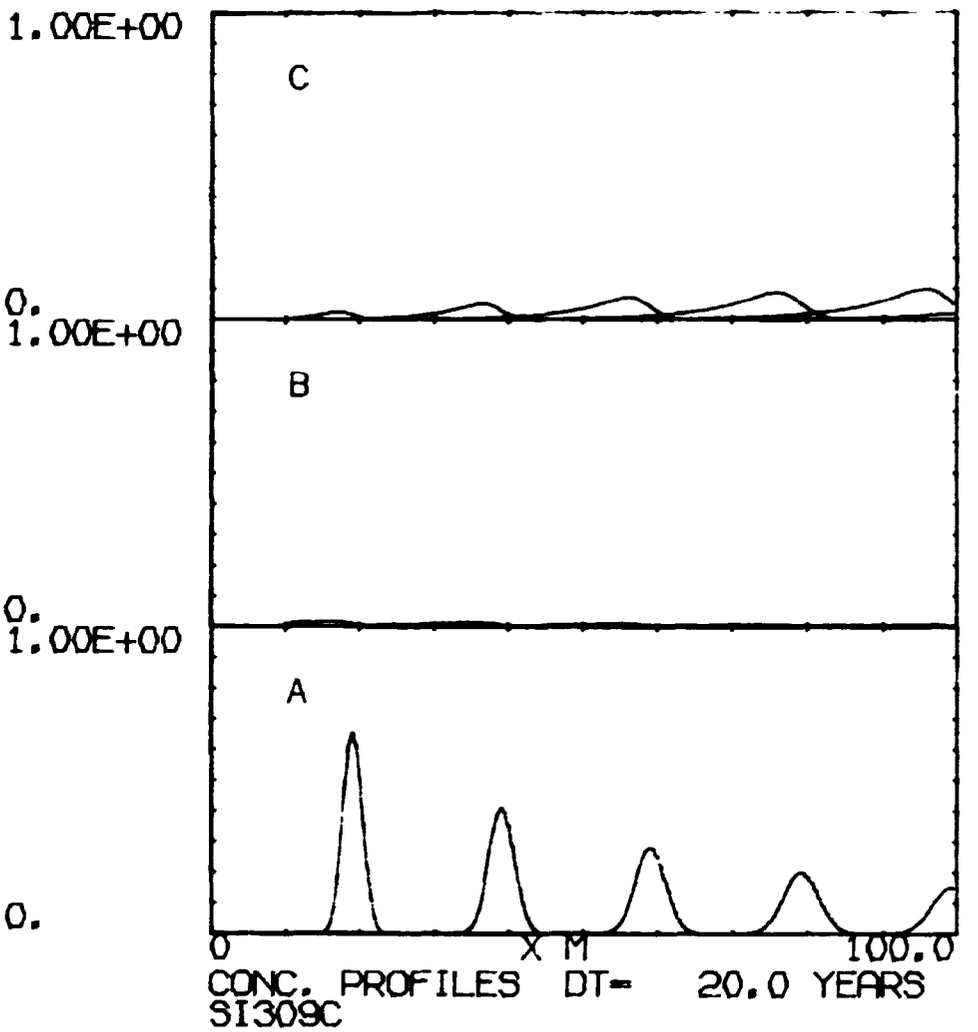

Figure 3-9. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.01$ y^{-1}, $k_2=0.1$ y^{-1}.

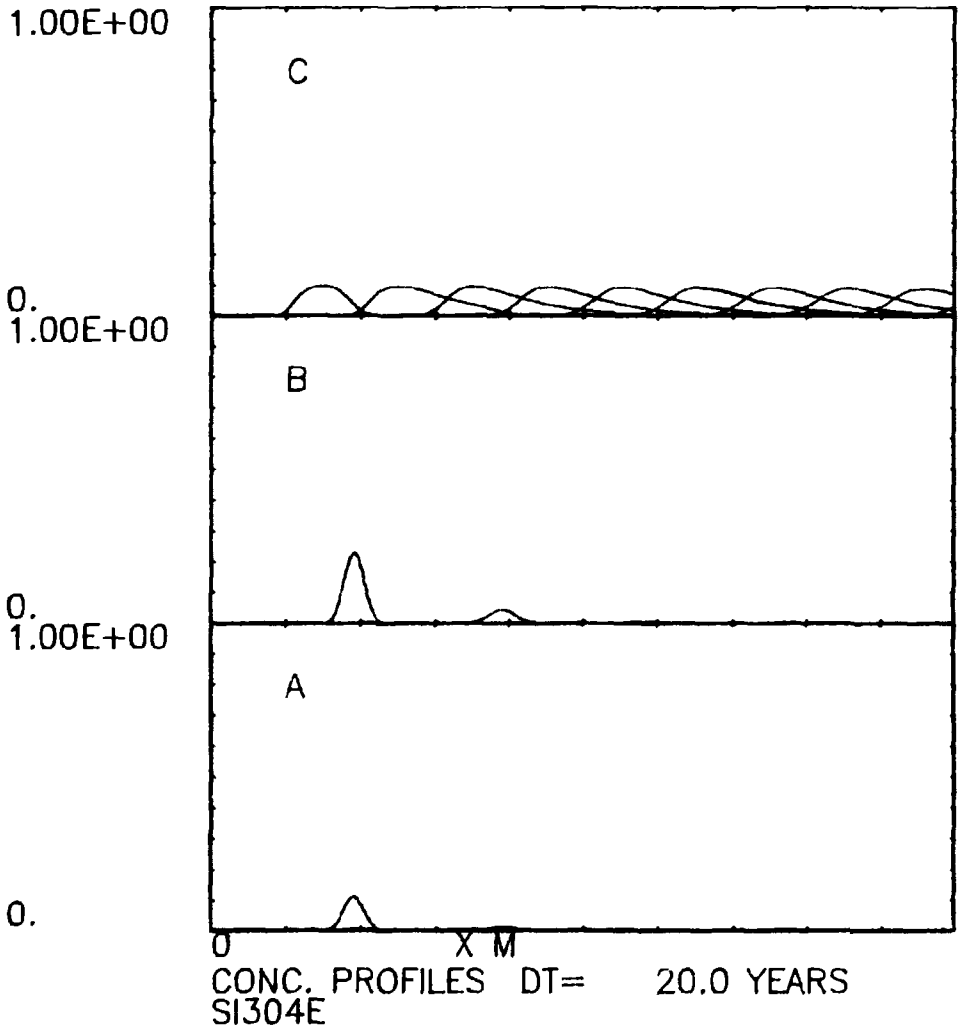

Figure 3-10. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_2=0.1$ y^{-1}.

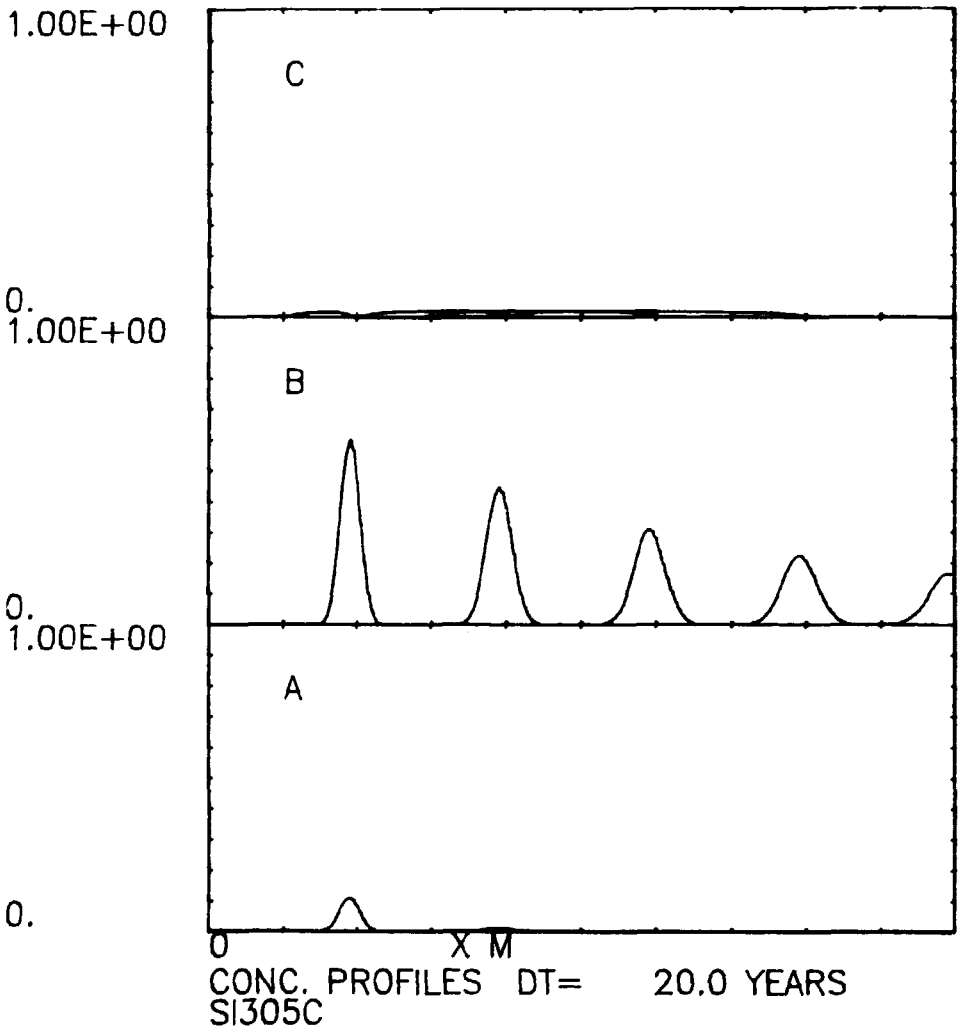

Figure 3-11. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1$ y^{-1}, $k_2=0.01$ y^{-1}.

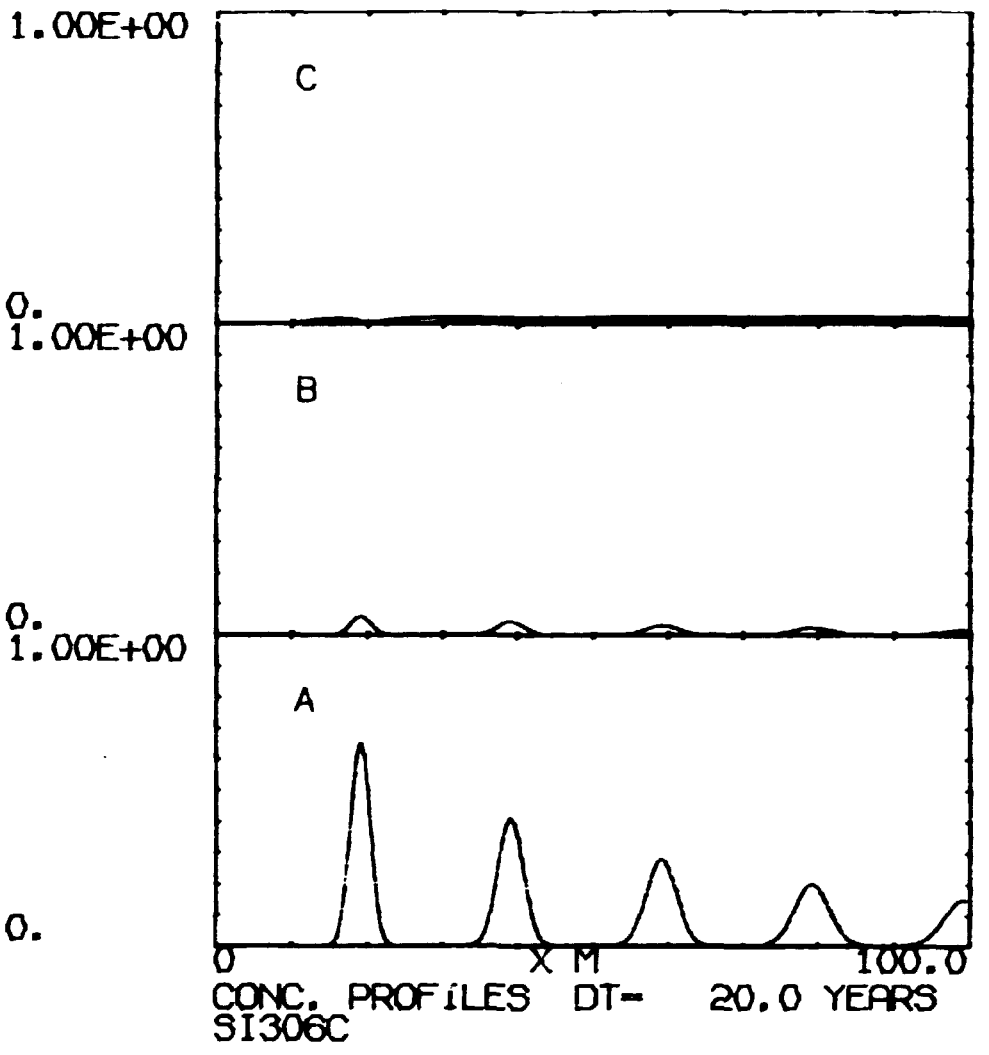

Figure 3-12. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.01$ y^{-1}, $k_2=0.1$ y^{-1}.

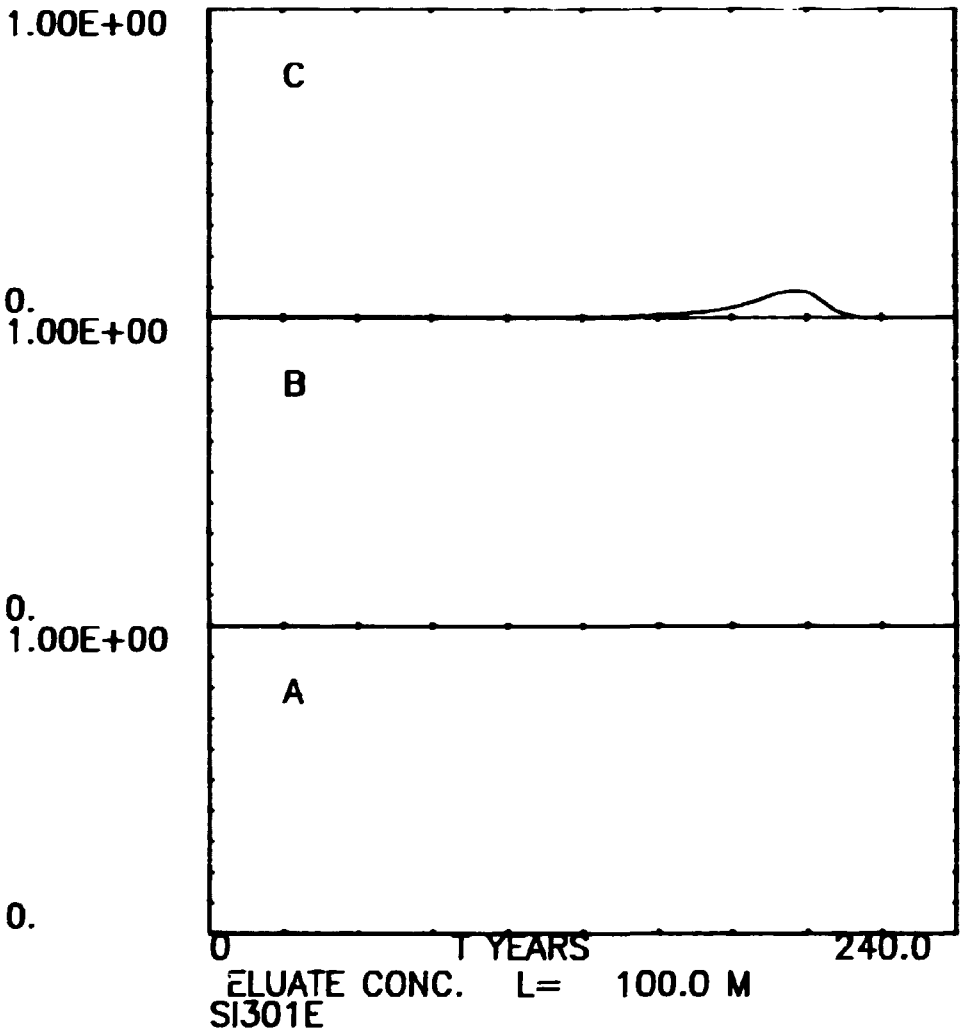

Figure 3-13. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_2=0.1$ y^{-1}.

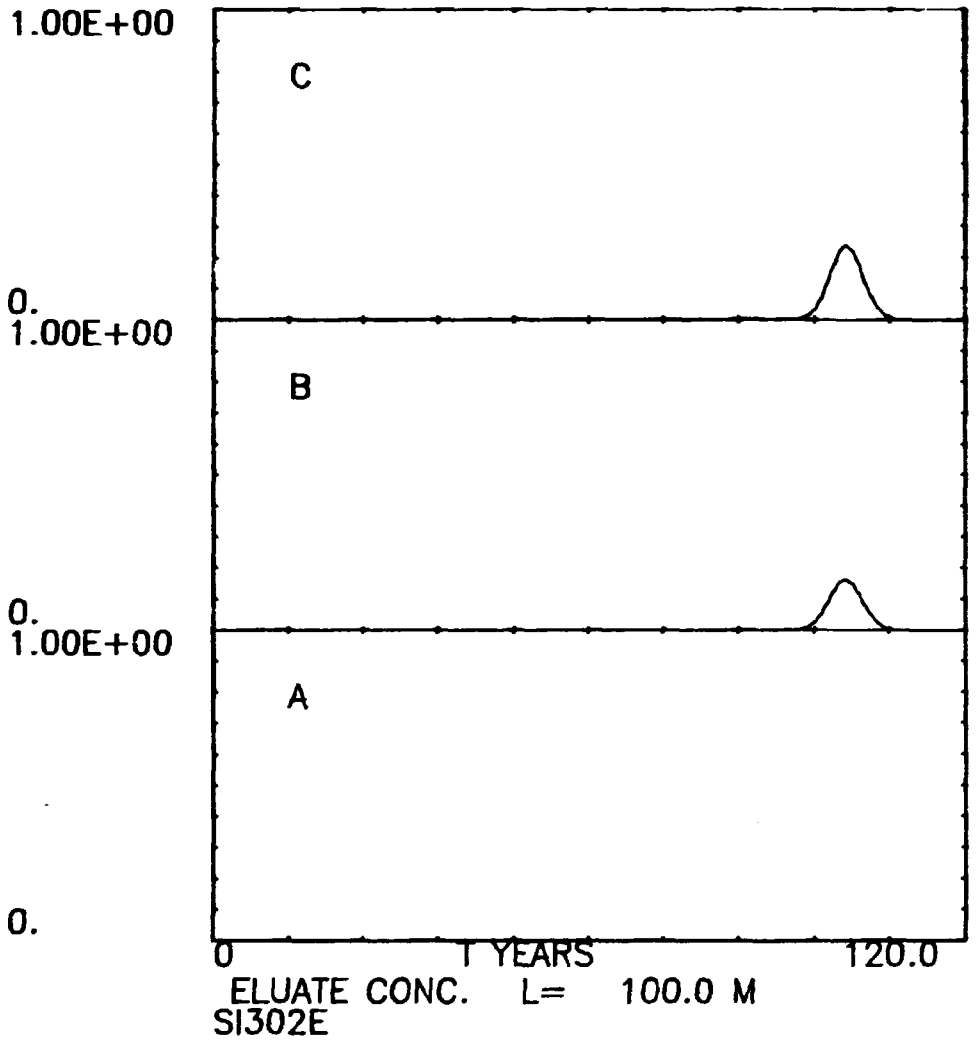

Figure 3-14. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1\ y^{-1}$, $k_2=0.01\ y^{-1}$.

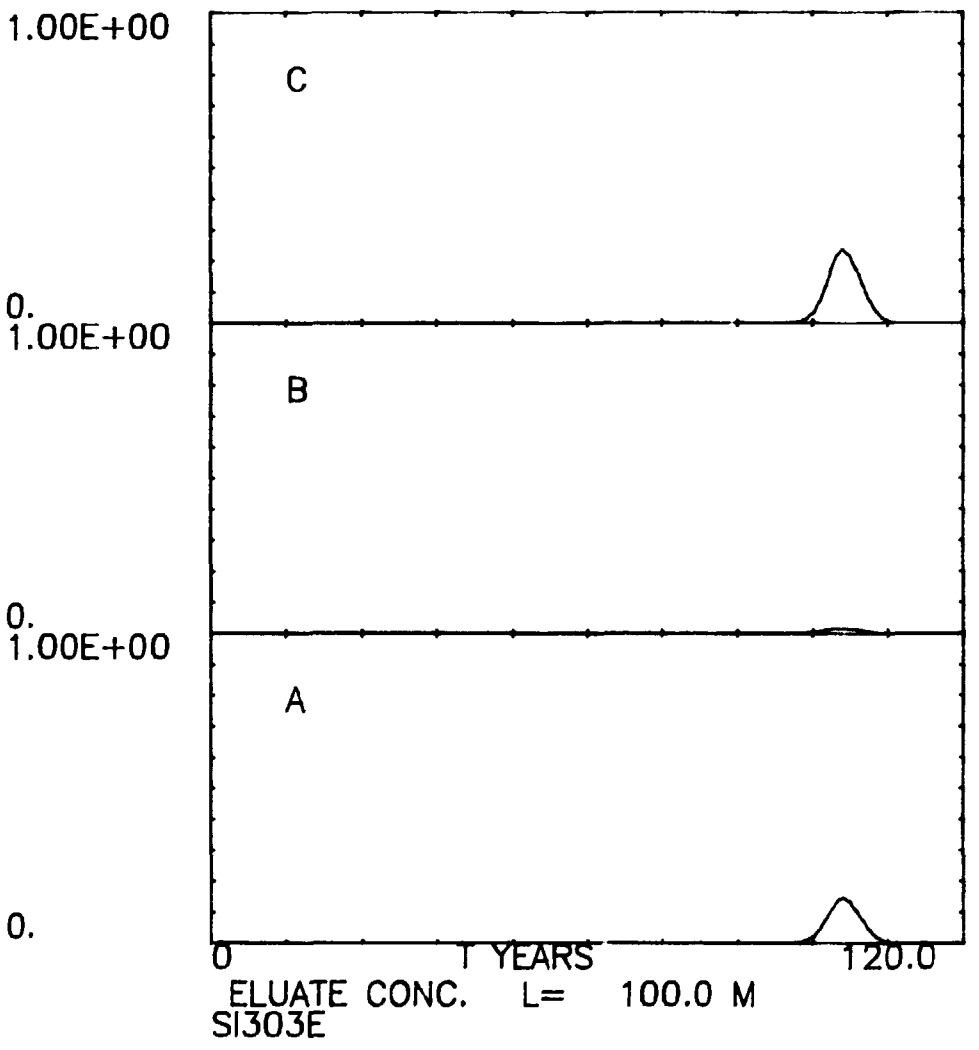

Figure 3-15. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, k_1=0.01 y^{-1}, k_2=0.1 y^{-1}.

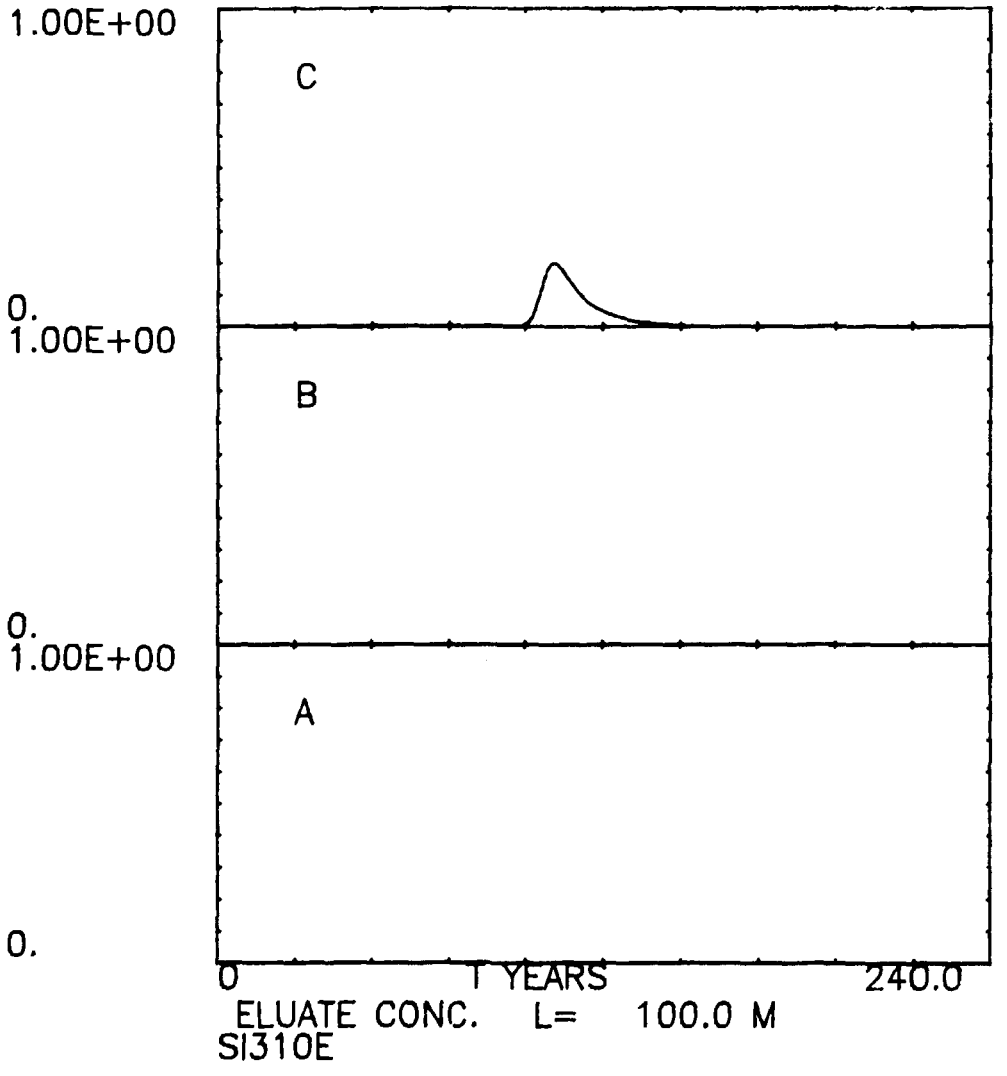

Figure 3-16. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}.

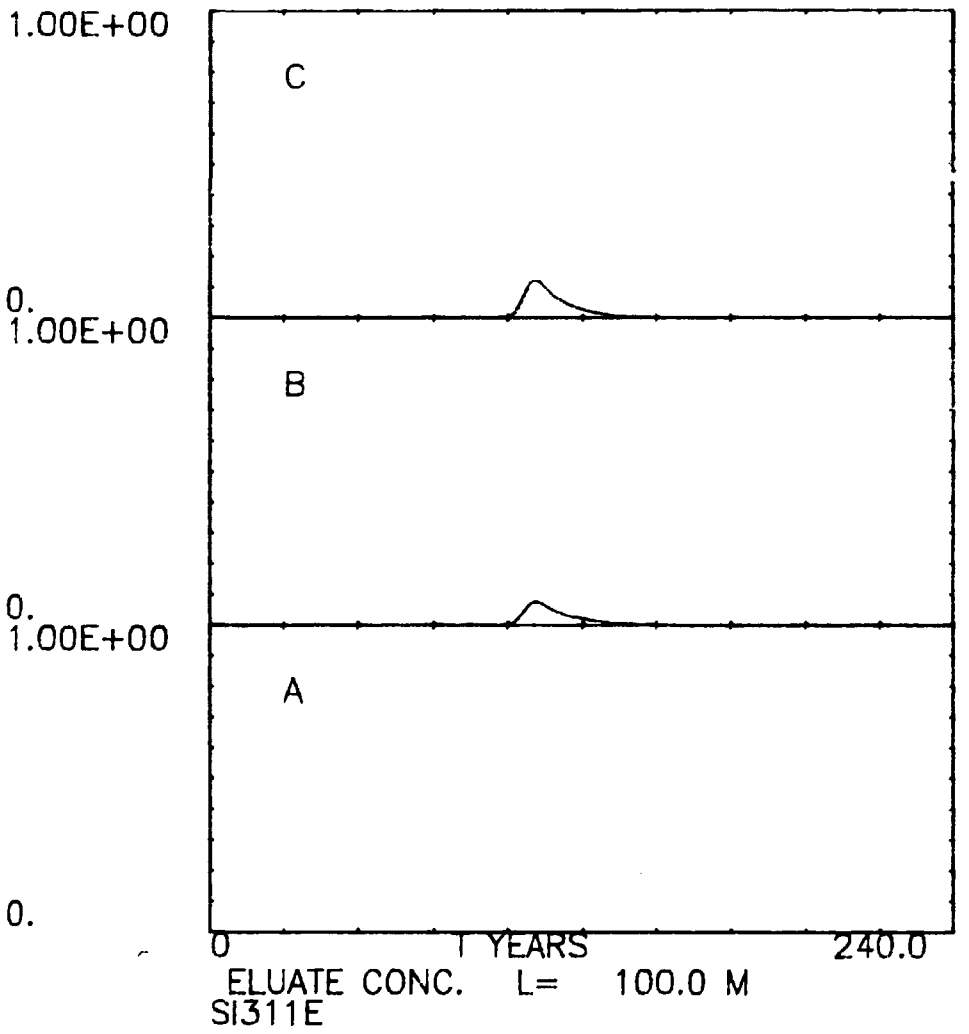

Figure 3-17. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1\ m\ y^{-1}$, $D=0.03\ m\ y^{-2}$, $k_1=0.1\ y^{-1}$, $k_{-1}=0.01\ y^{-1}$.

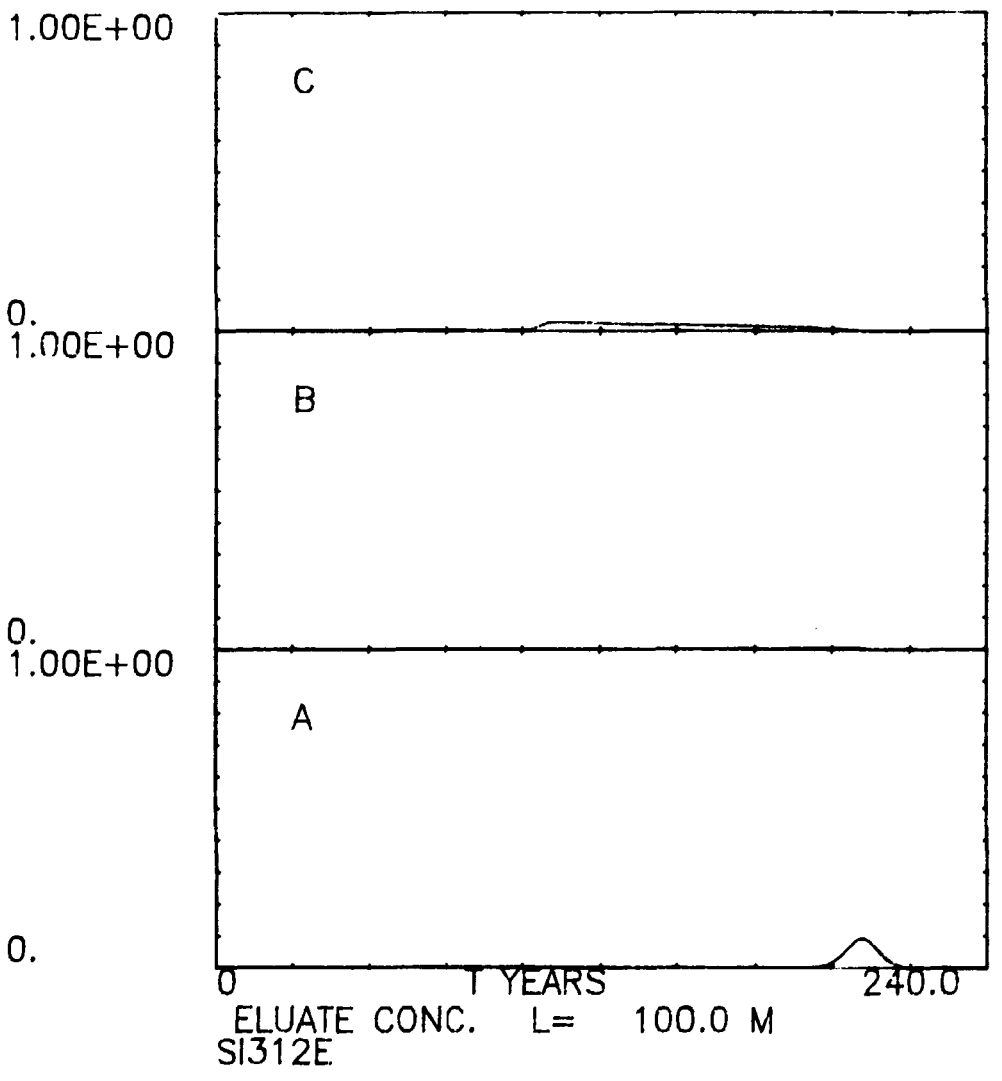

Figure 3-18. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.01$ y^{-1}, $k_{-1}=0.1$ y^{-1}.

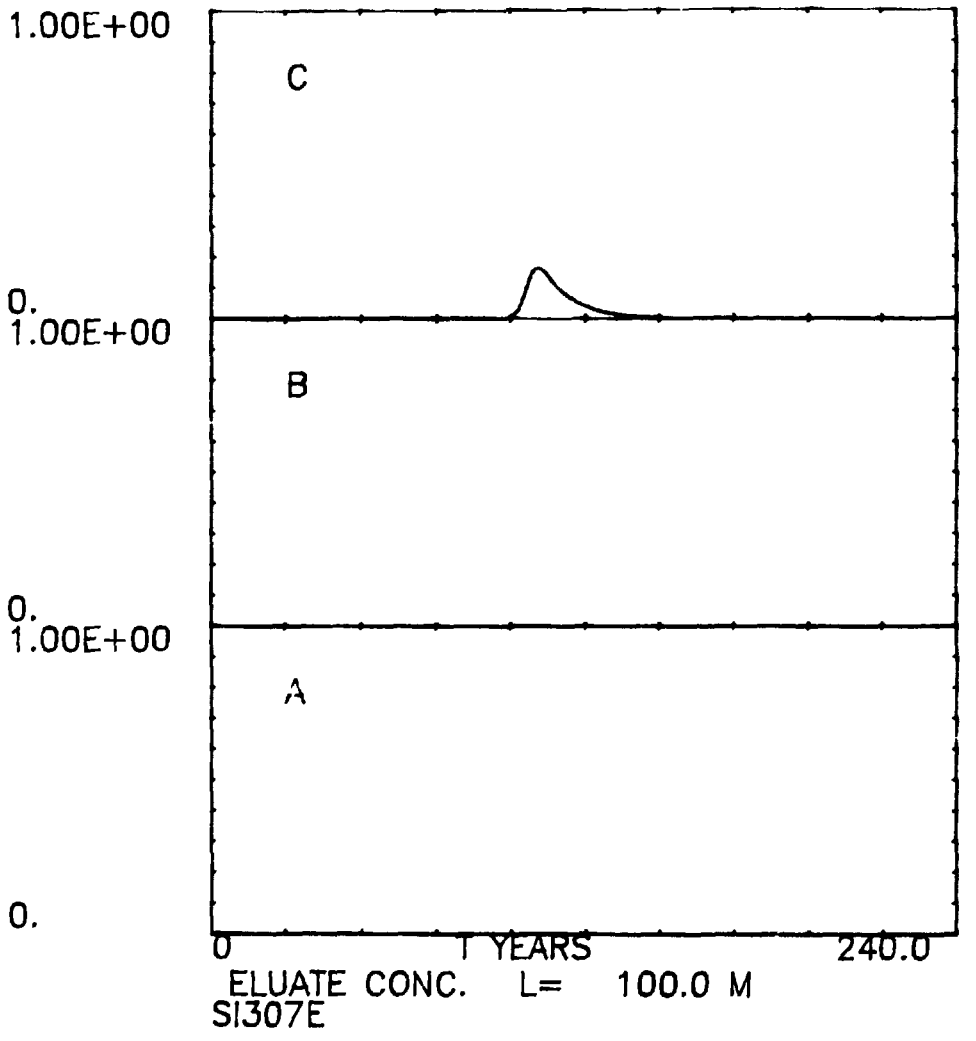

Figure 3-19. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_2=0.1$ y^{-1}.

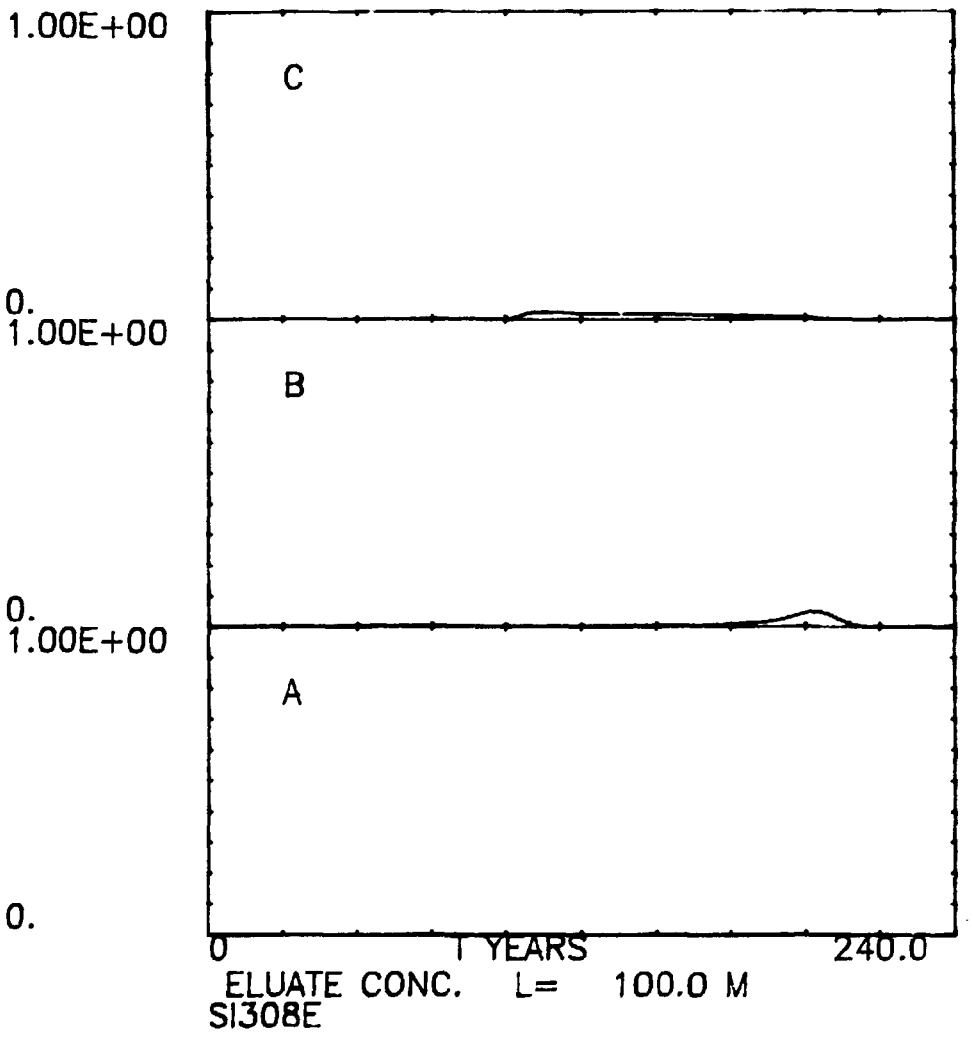

Figure 3-2C. $R_f(A)=R_f(C)=1, R_f(B)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1\ y^{-1}$, $k_2=0.01\ y^{-1}$.

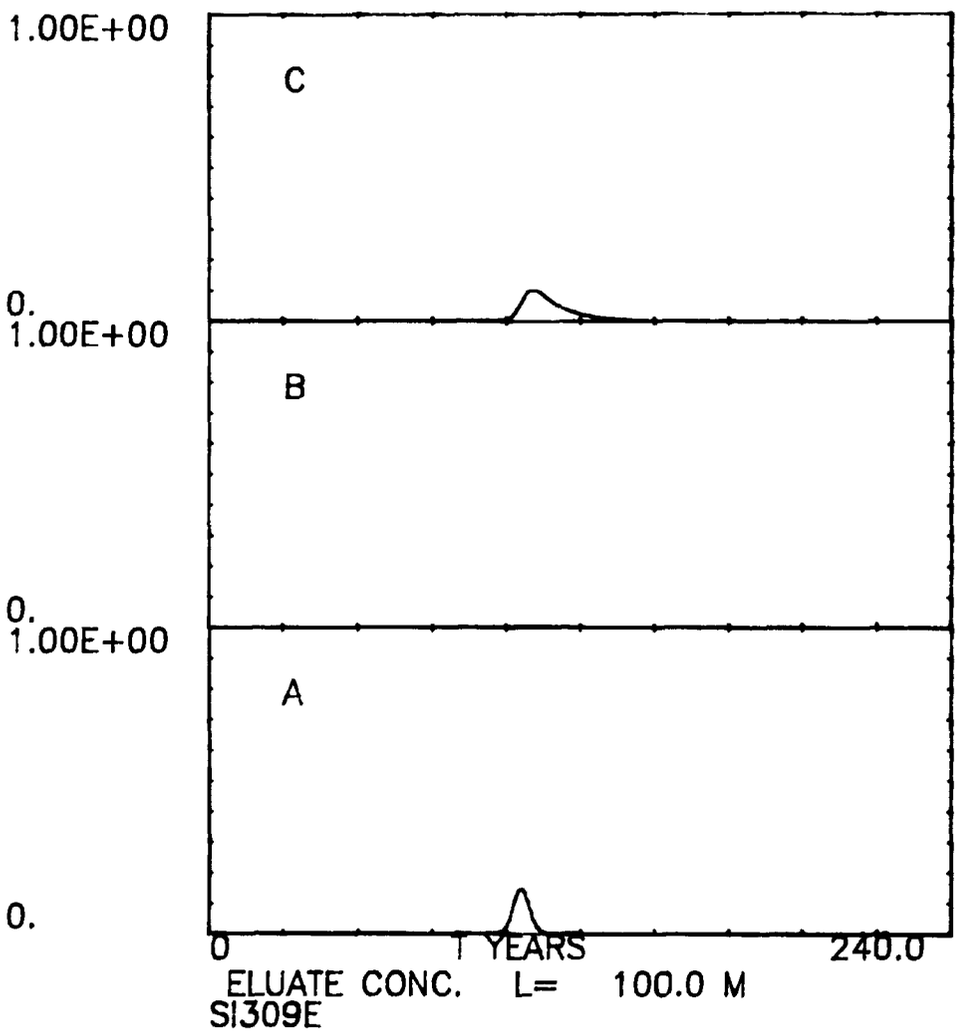

Figure 3-21. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.01$ y^{-1}, $k_2=0.1$ y^{-1}.

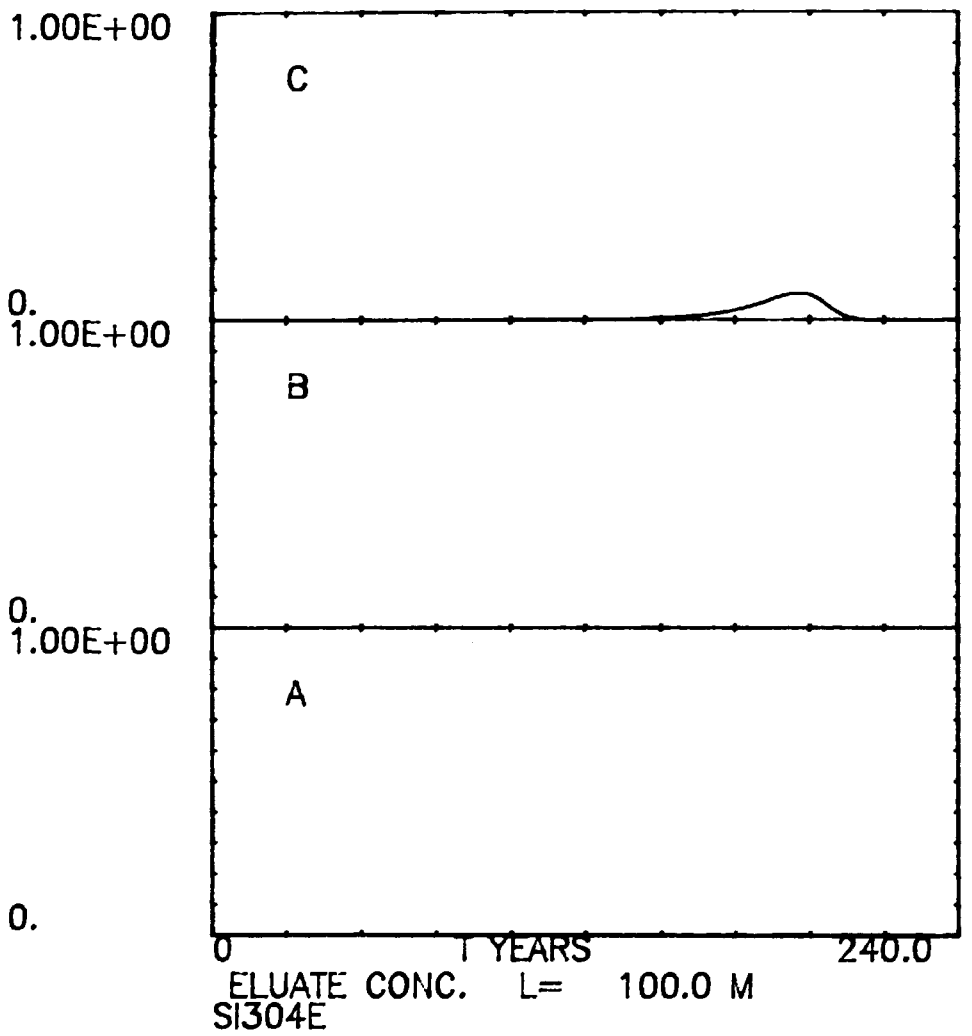

Figure 3-22. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_2=0.1$ y^{-1}.

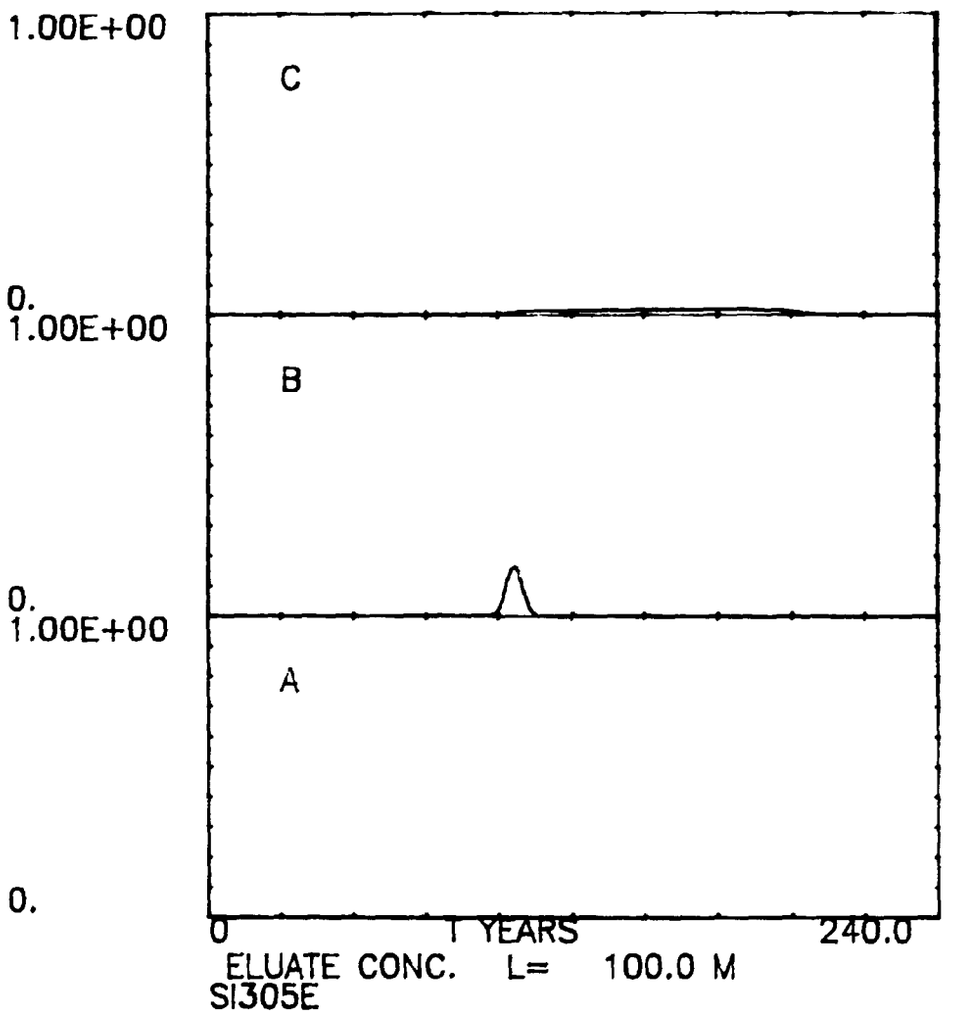

Figure 3-23. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1$ y^{-1}, $k_2=0.01$ y^{-1}.

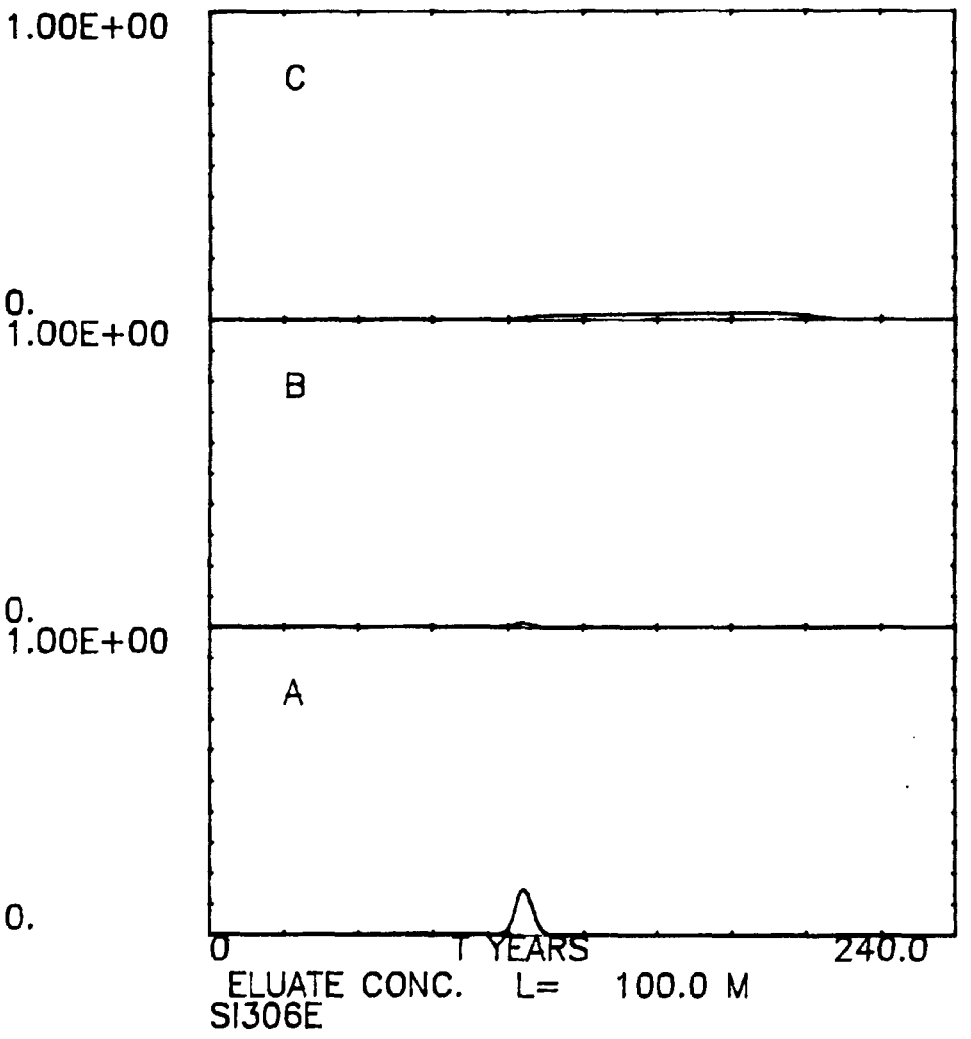

Figure 3-24. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, V=1 m y^{-1}, D 0.03 m y^{-2}, $k_1=0.01$ y^{-1}, $k_2=0.1$ y^{-1}.

FIGURES FOR SECTION 4.4

$$A \rightleftarrows B$$

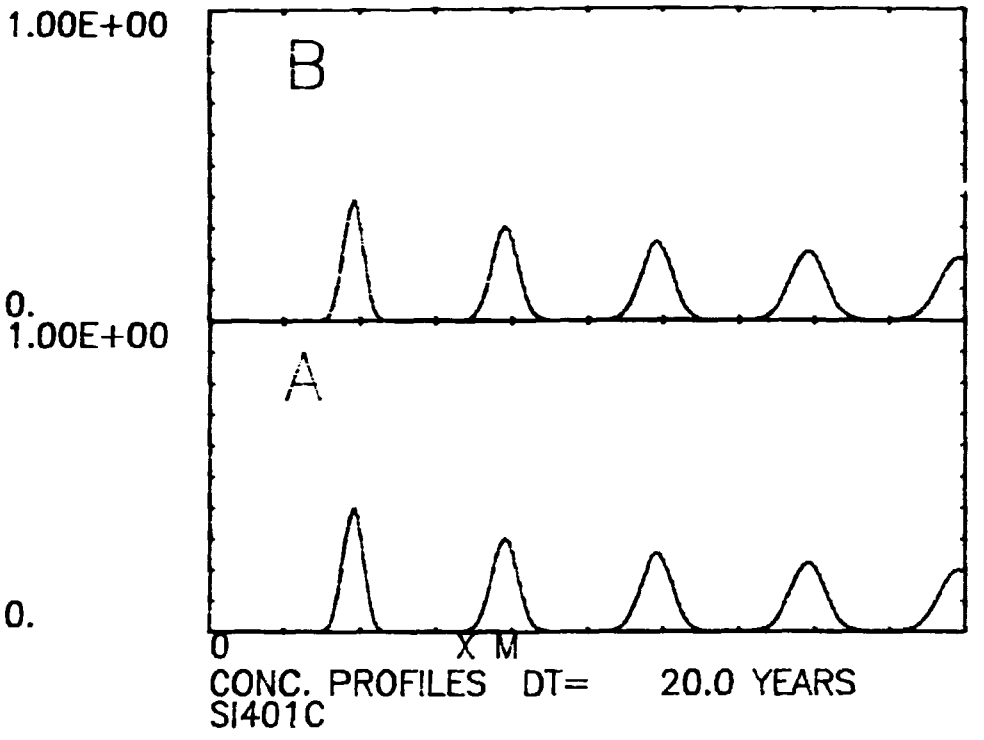

Figure 4-1. $R_f(A)=R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}.

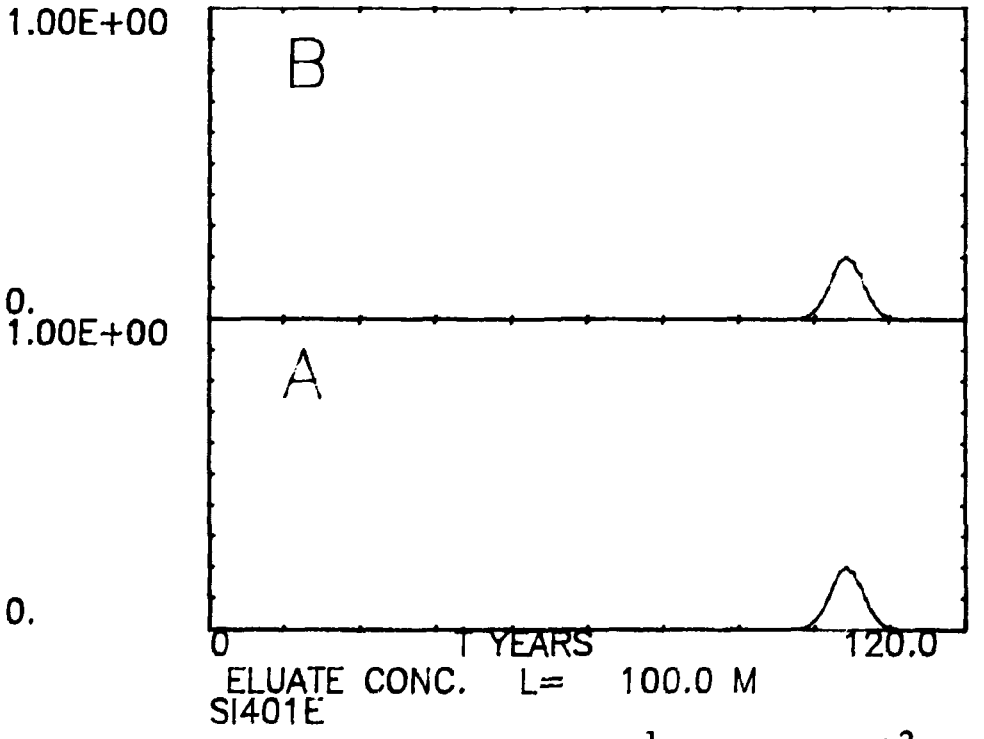

Figure 4-2. $R_f(A)=R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}.

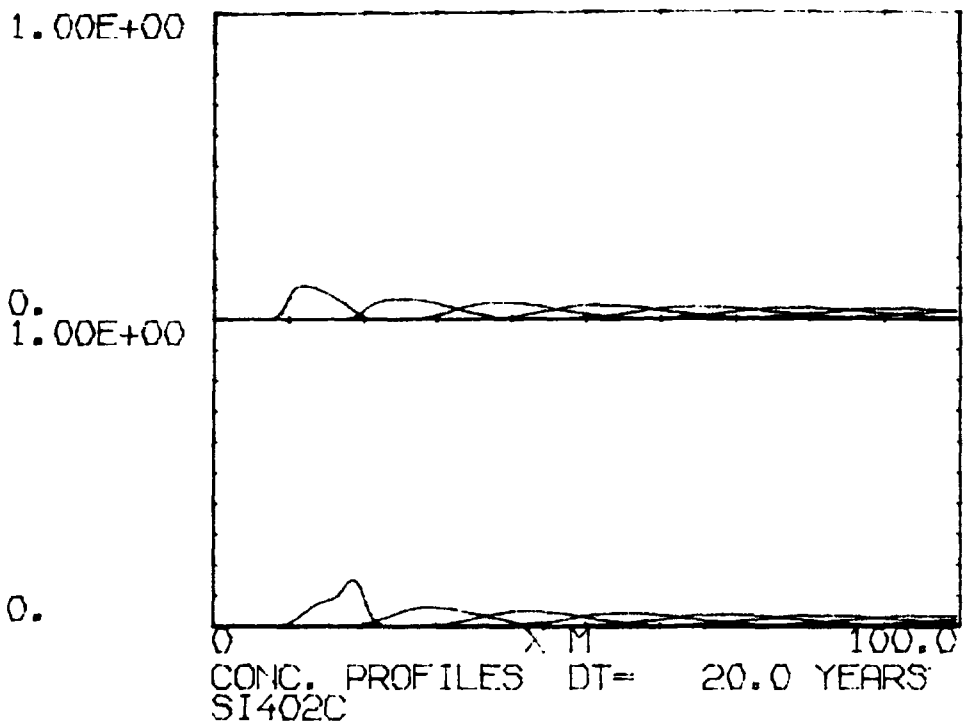

Figure 4-3. $R_f(A)=1$, $R_f(B)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}.

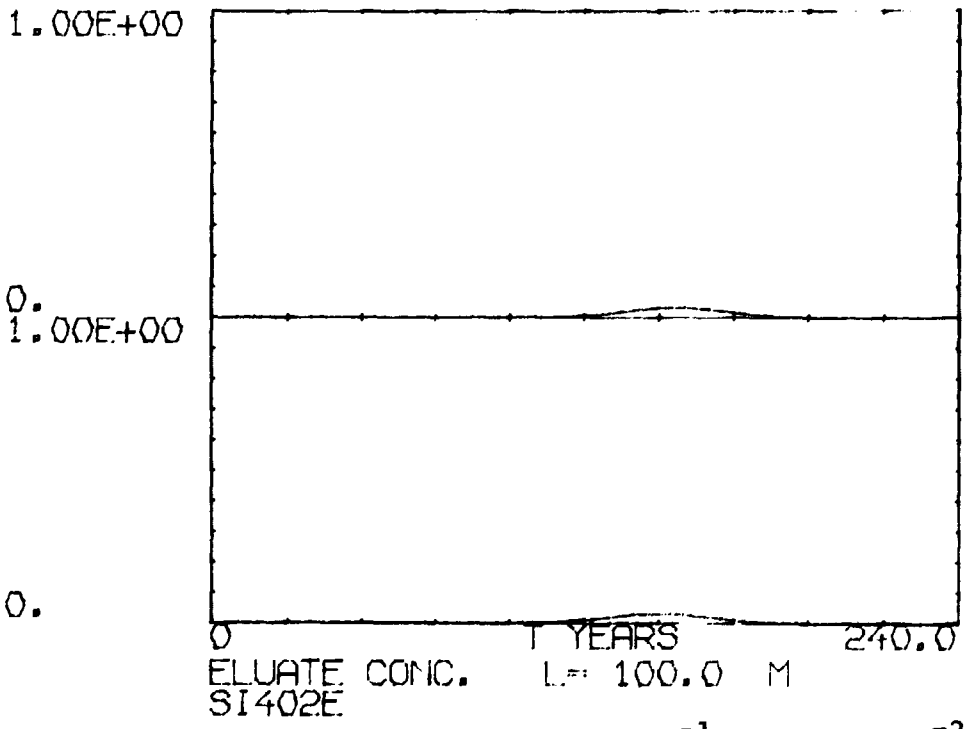

Figure 4-4. $R_f(A)=1$, $R_f(B)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}.

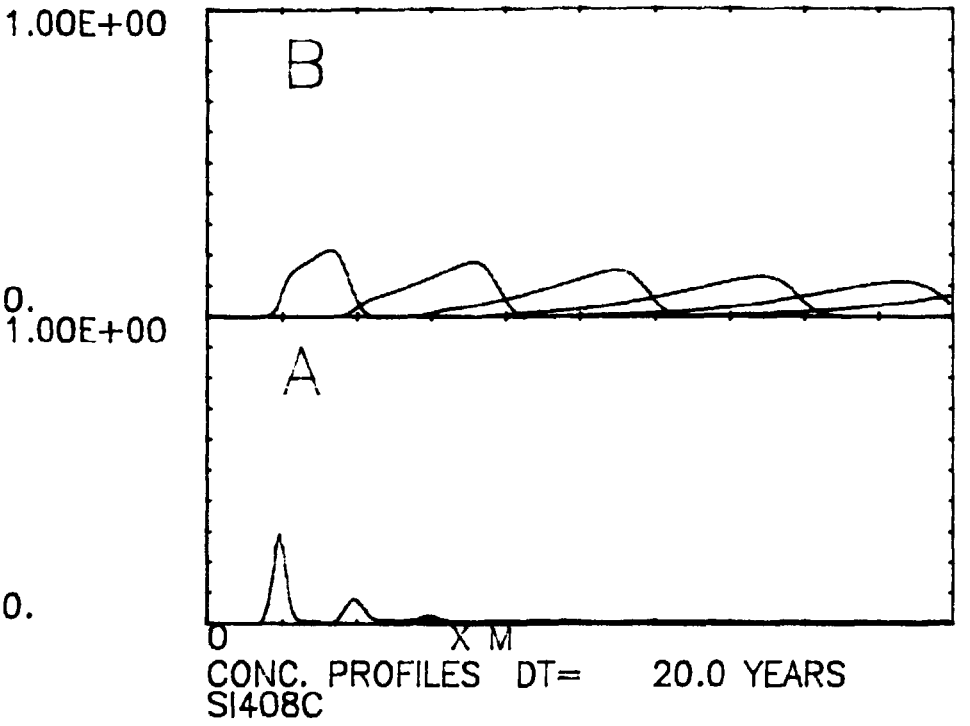

Figure 4-5. $R_f(A)=2$, $R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1\ y^{-1}$, $k_{-1}=0.01\ y^{-1}$.

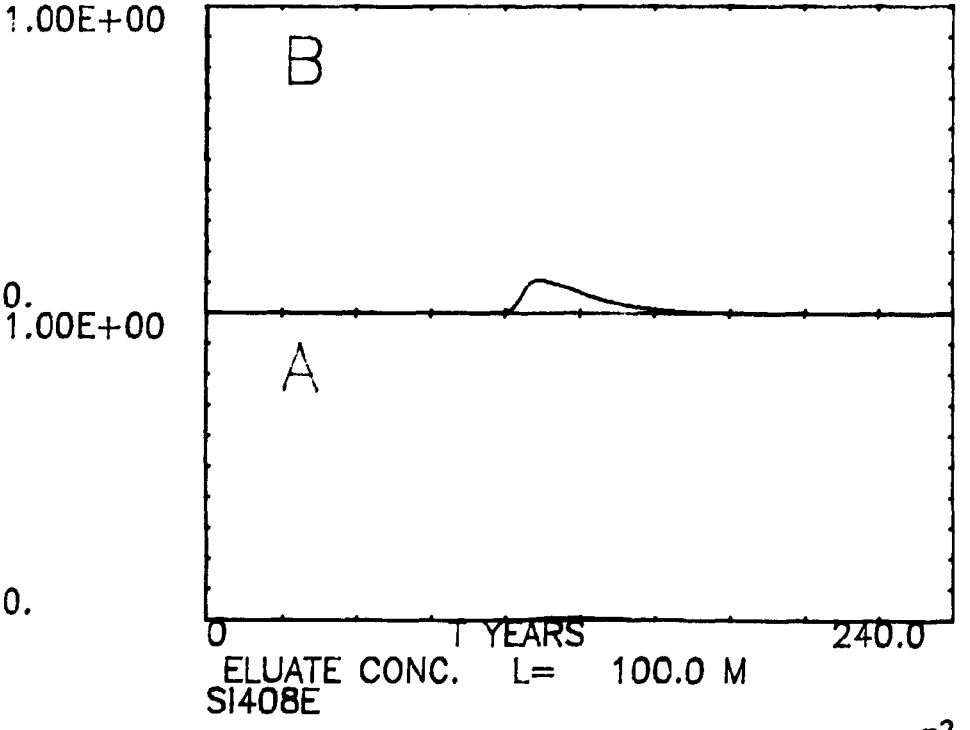

Figure 4-6. $R_f(A)=2$, $R_f(B)=1$, V=1 m y_{-1}, D=0.03 m y^{-2}, $k_1=0.1\ y^{-1}$, $k_{-1}=0.01\ y^{-1}$.

FIGURES FOR SECTION 4.5

$$A \rightleftarrows B \rightarrow C$$

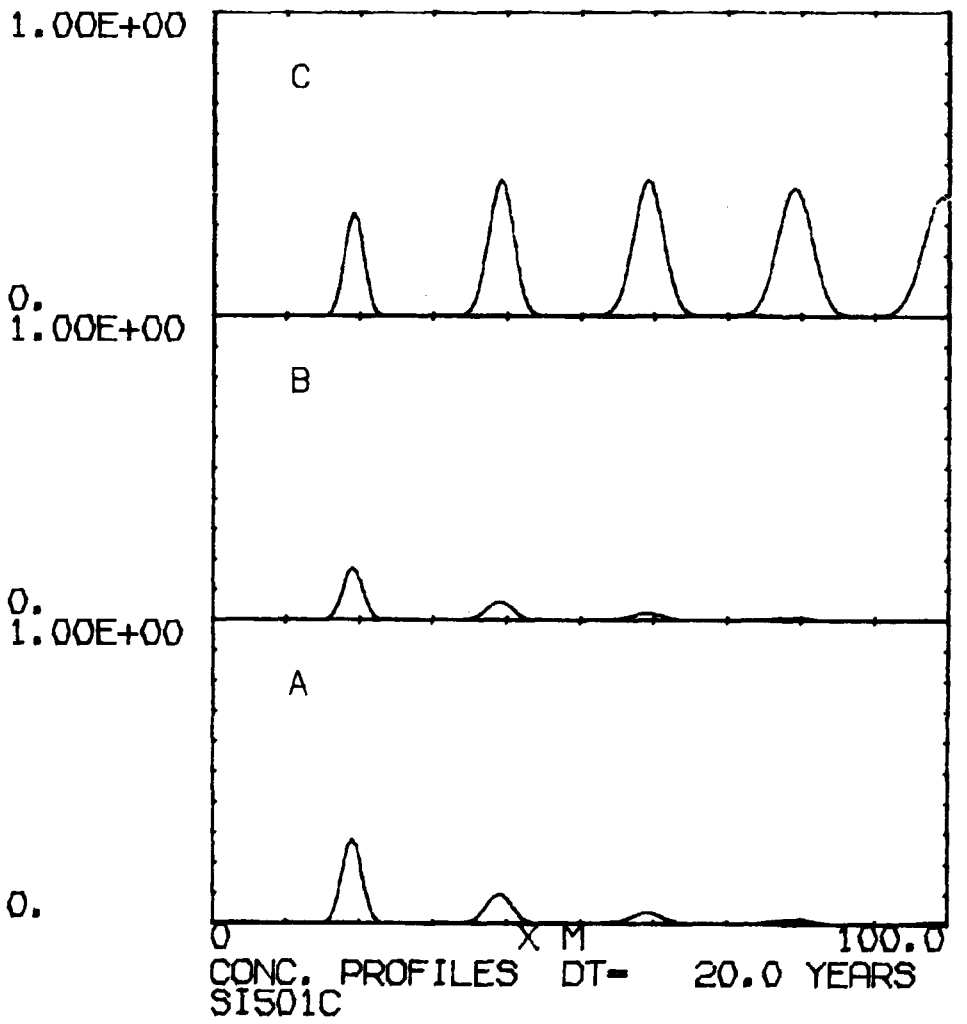

Figure 5-1. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

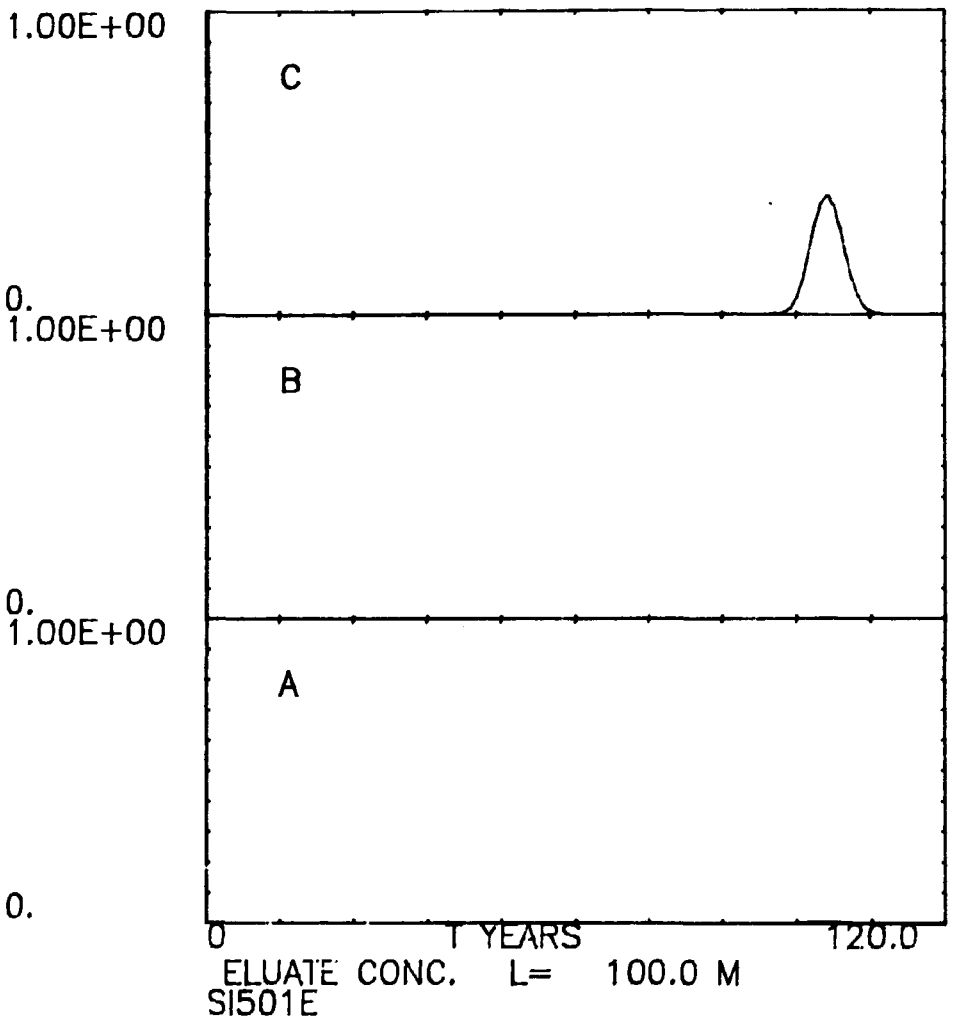

Figure 5-2. $R_f(A)=R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

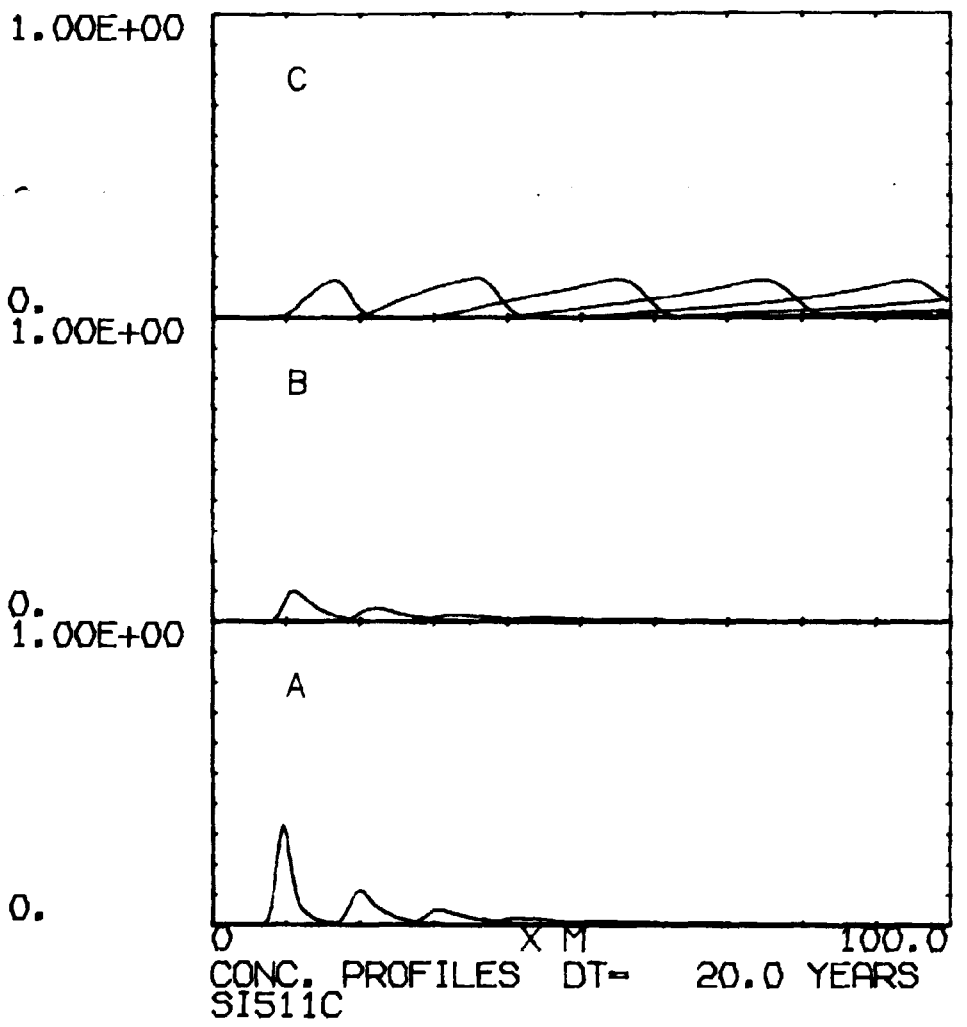

Figure 5-3. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

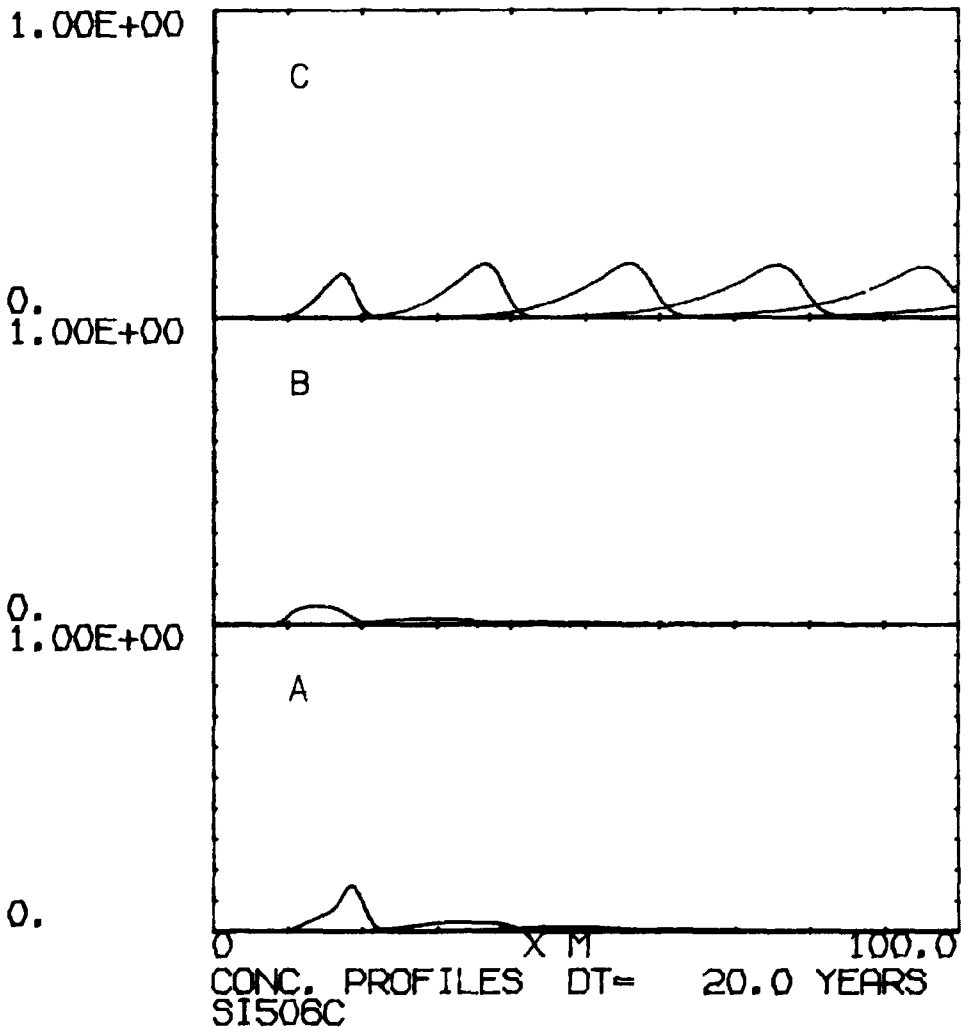

Figure 5-4. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

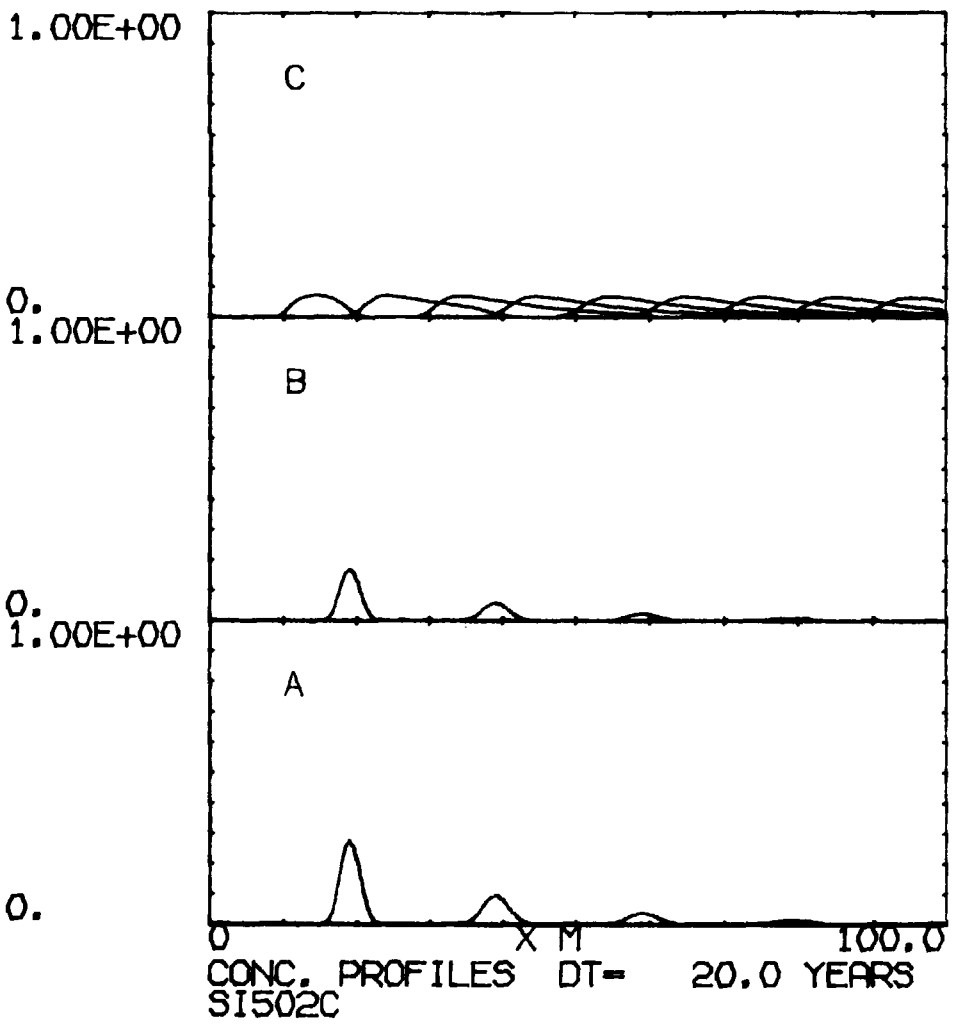

Figure 5-5. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

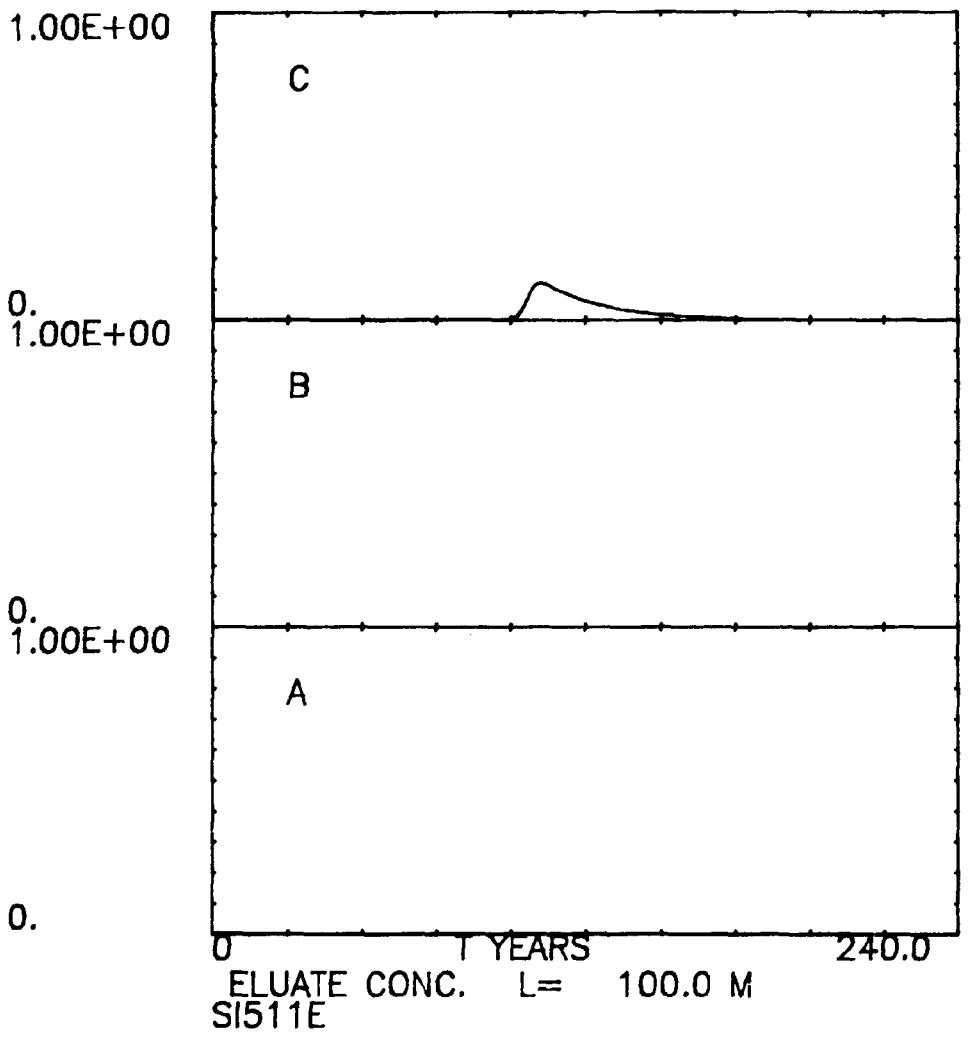

Figure 5-6. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

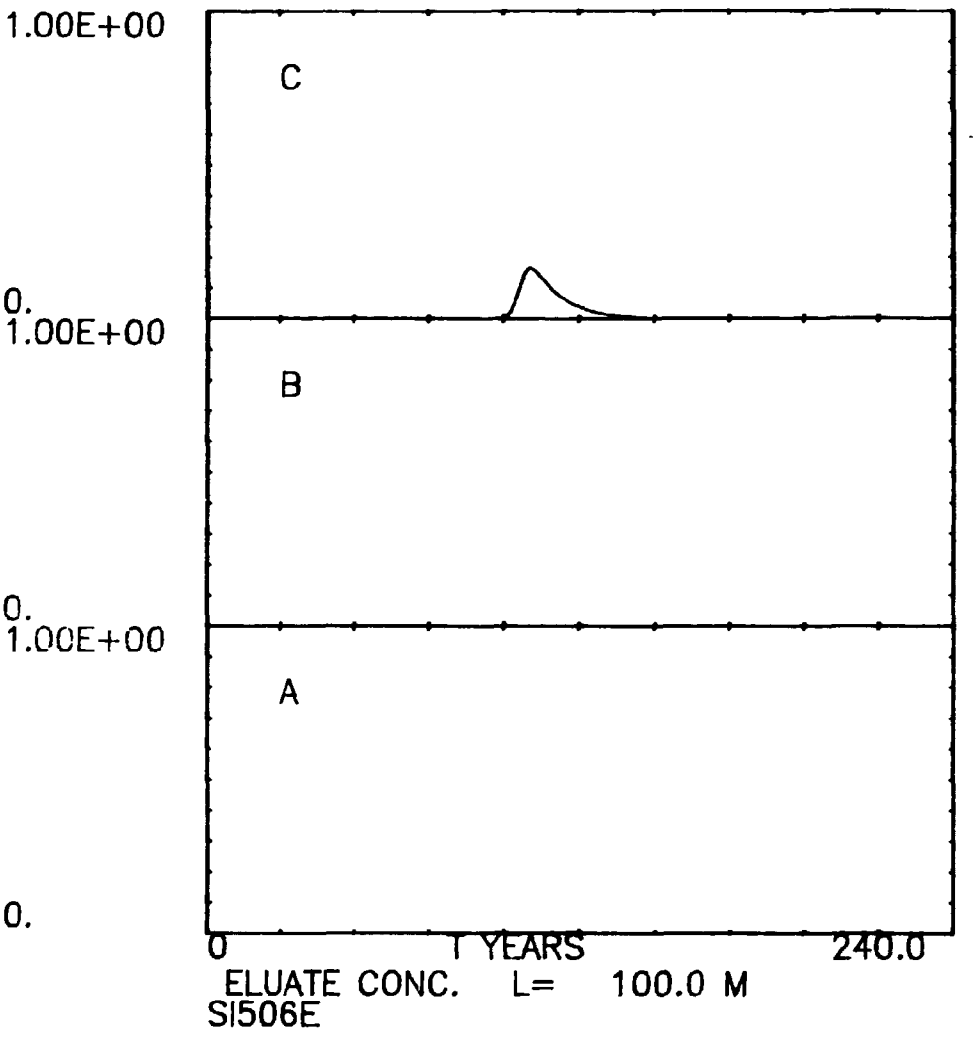

Figure 5-7. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=0,1$ y^{-1}.

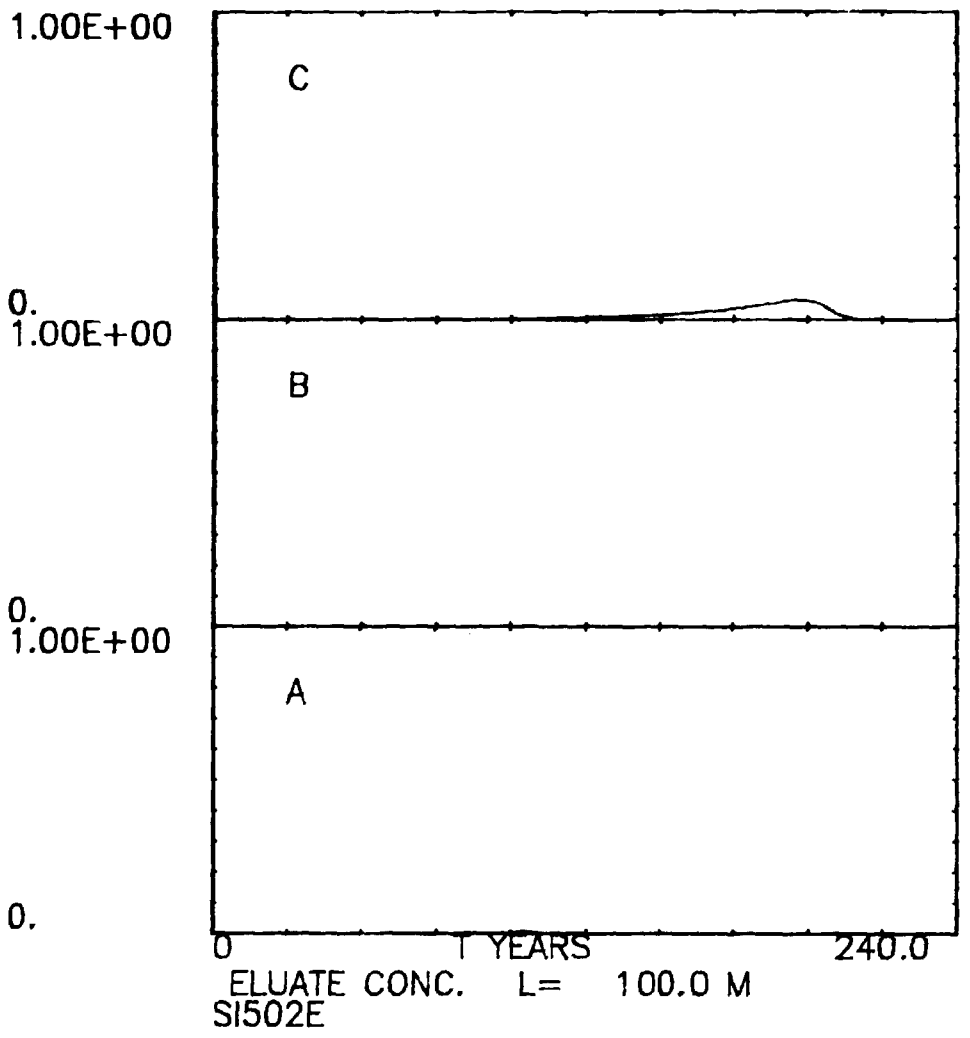

Figure 5-8. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

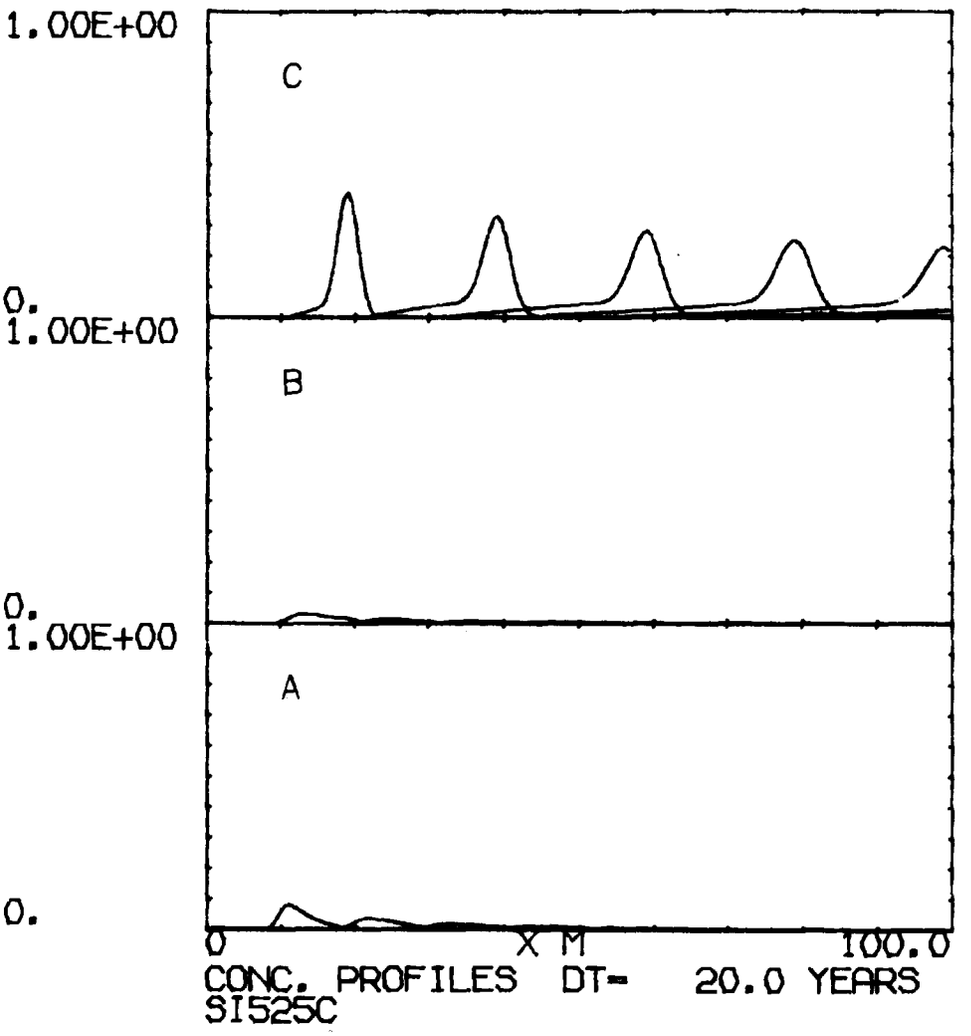

Figure 5-9. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

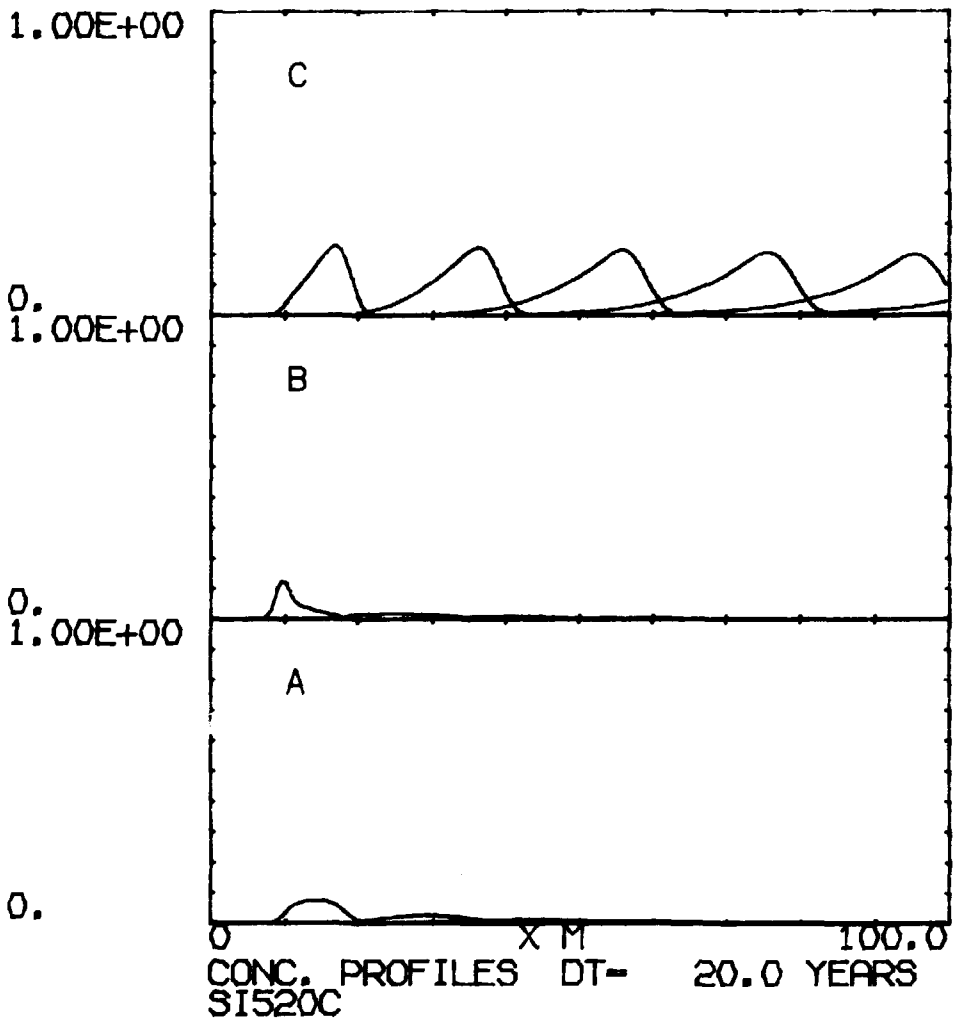

Figure 5-10. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

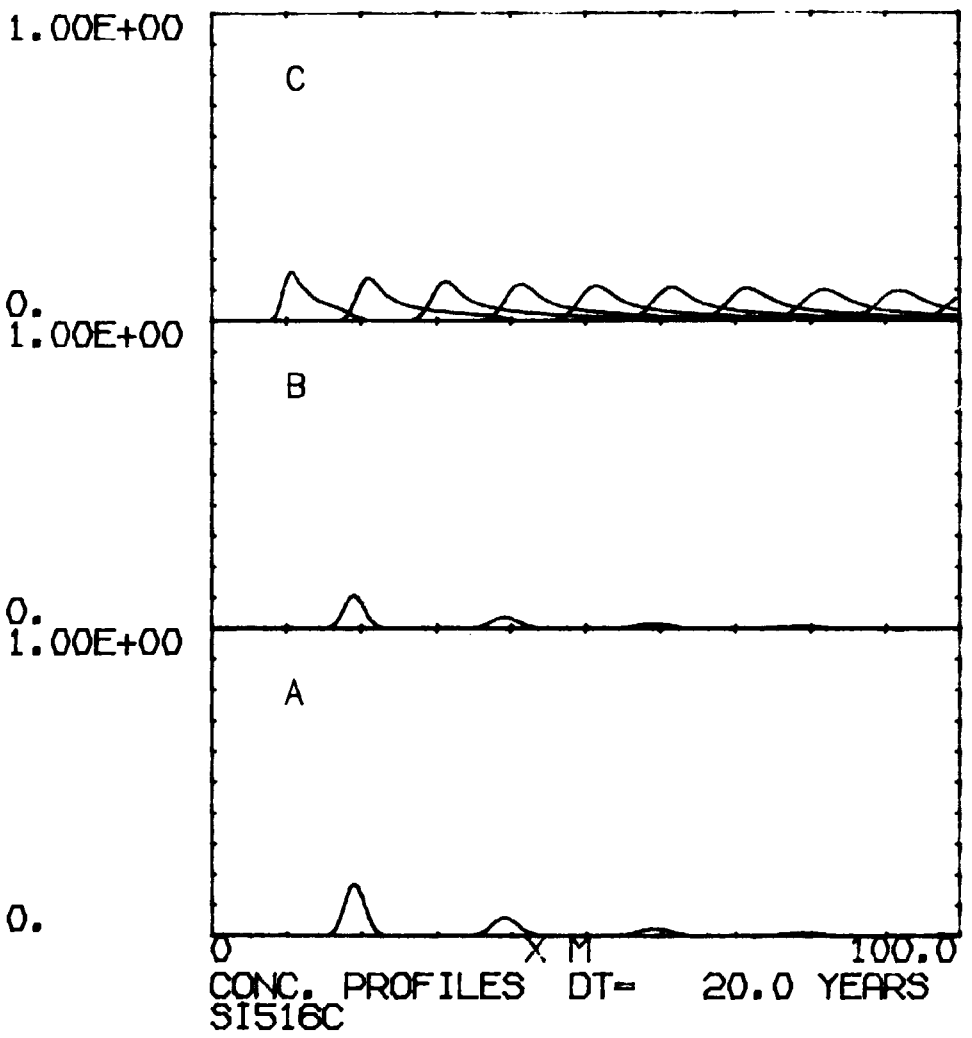

Figure 5-11. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

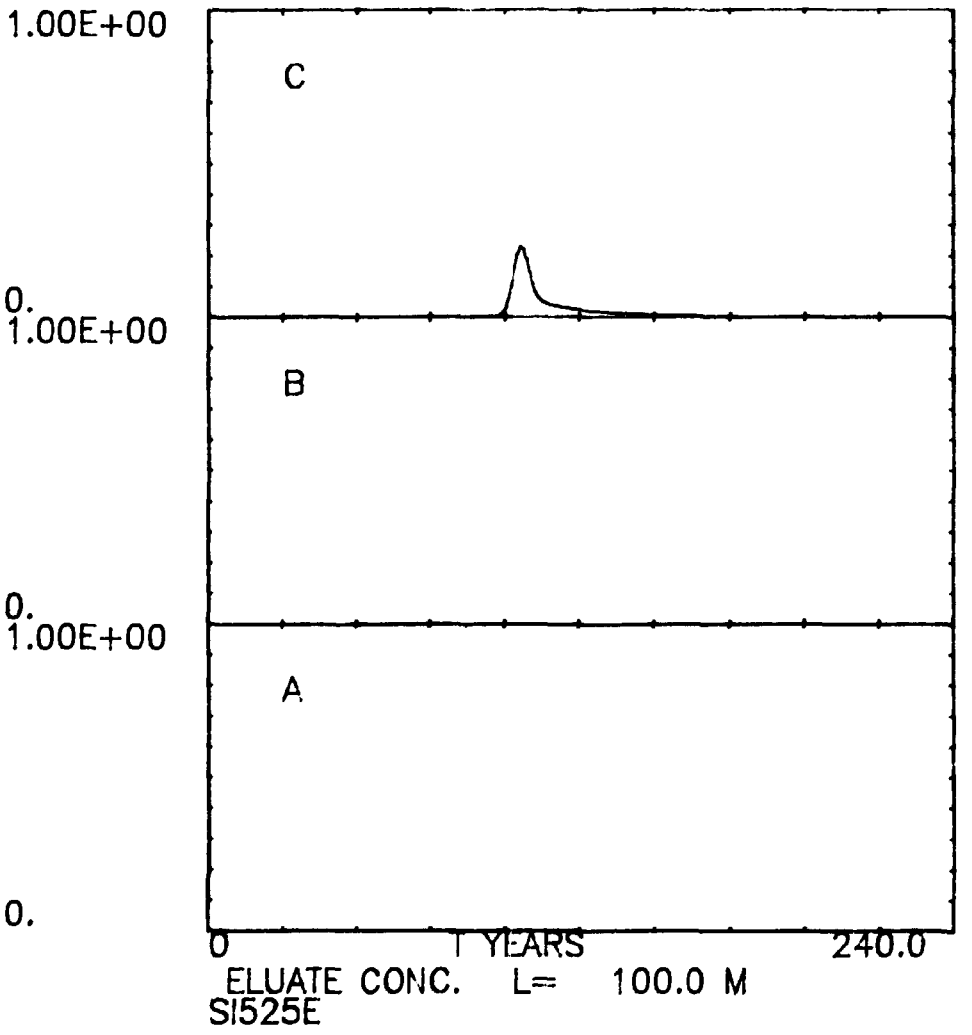

Figure 5-12. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

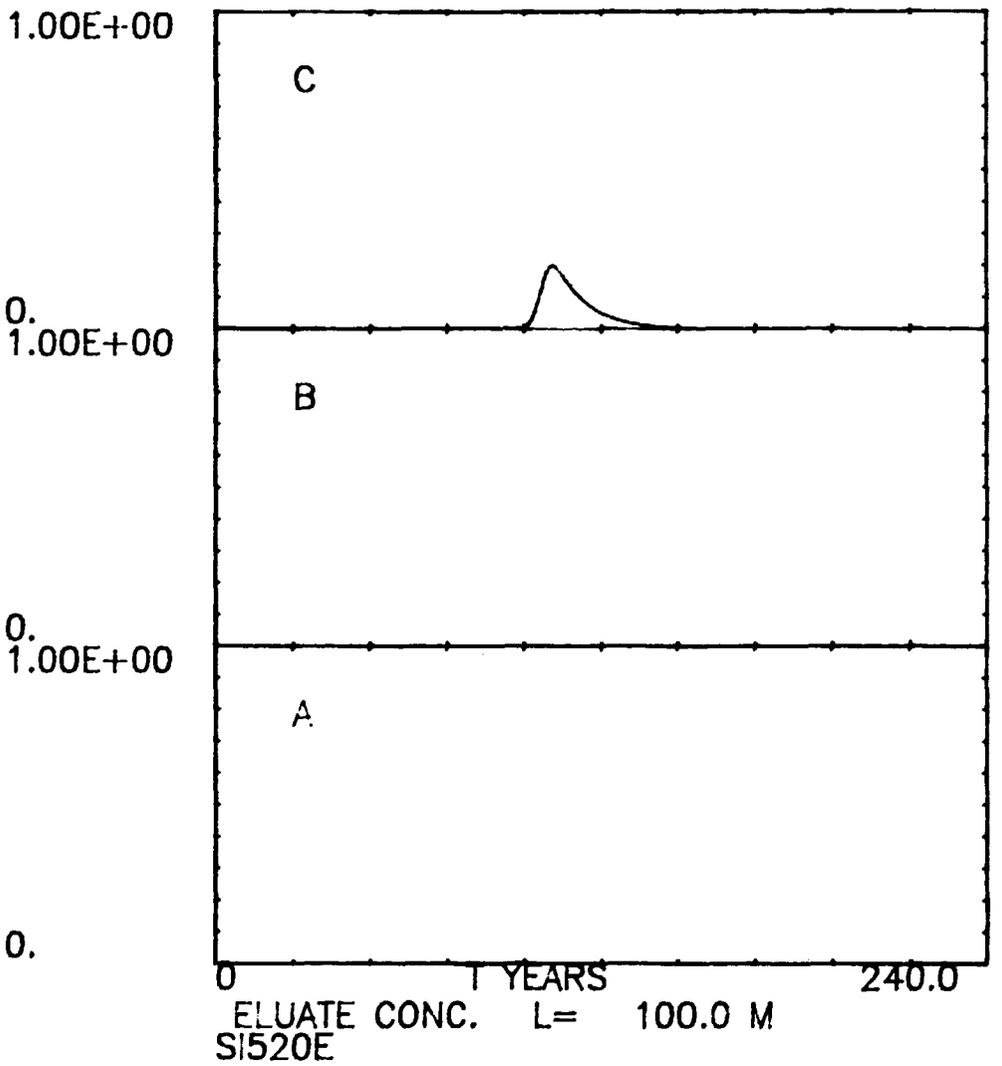

Figure 5-13. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

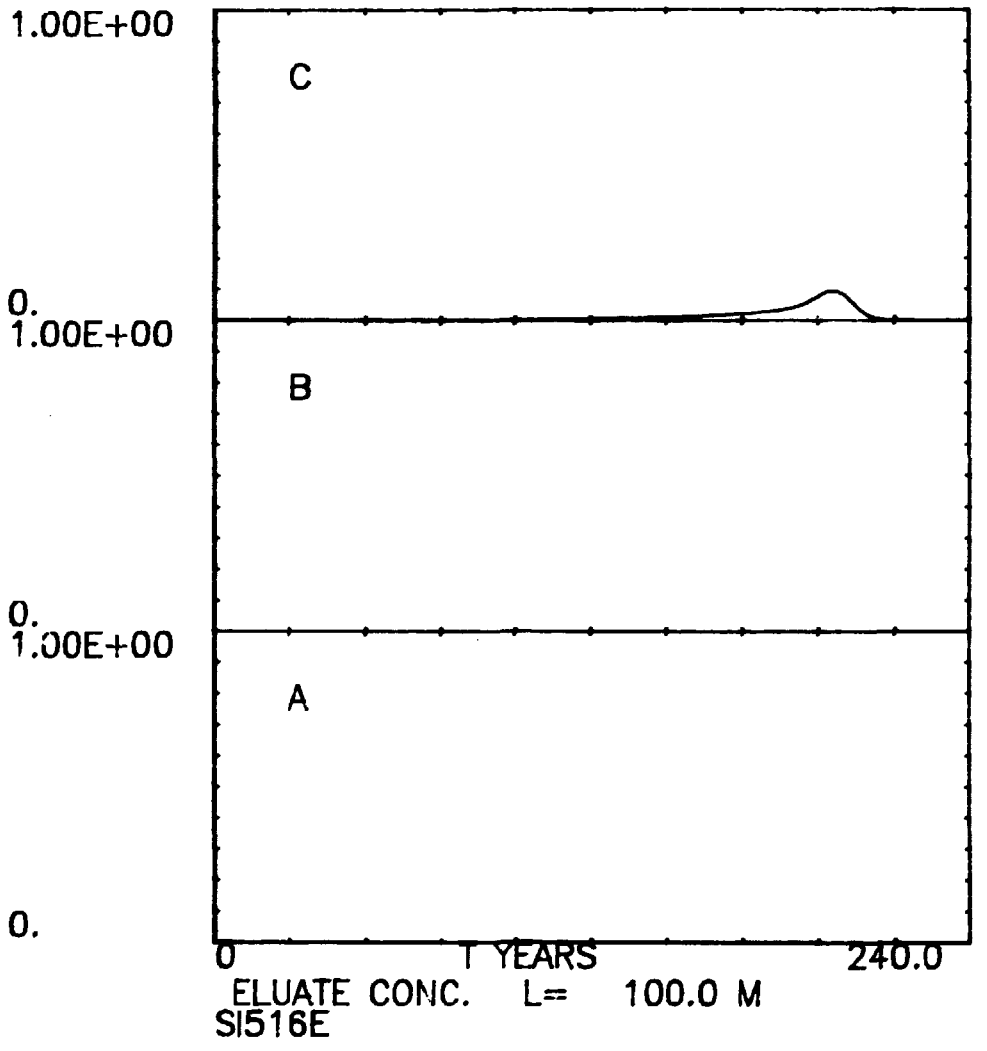

Figure 5-14. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=0.1$ y^{-1}.

FIGURES FOR SECTION 4.6

$$A \rightleftarrows B \rightleftarrows C$$

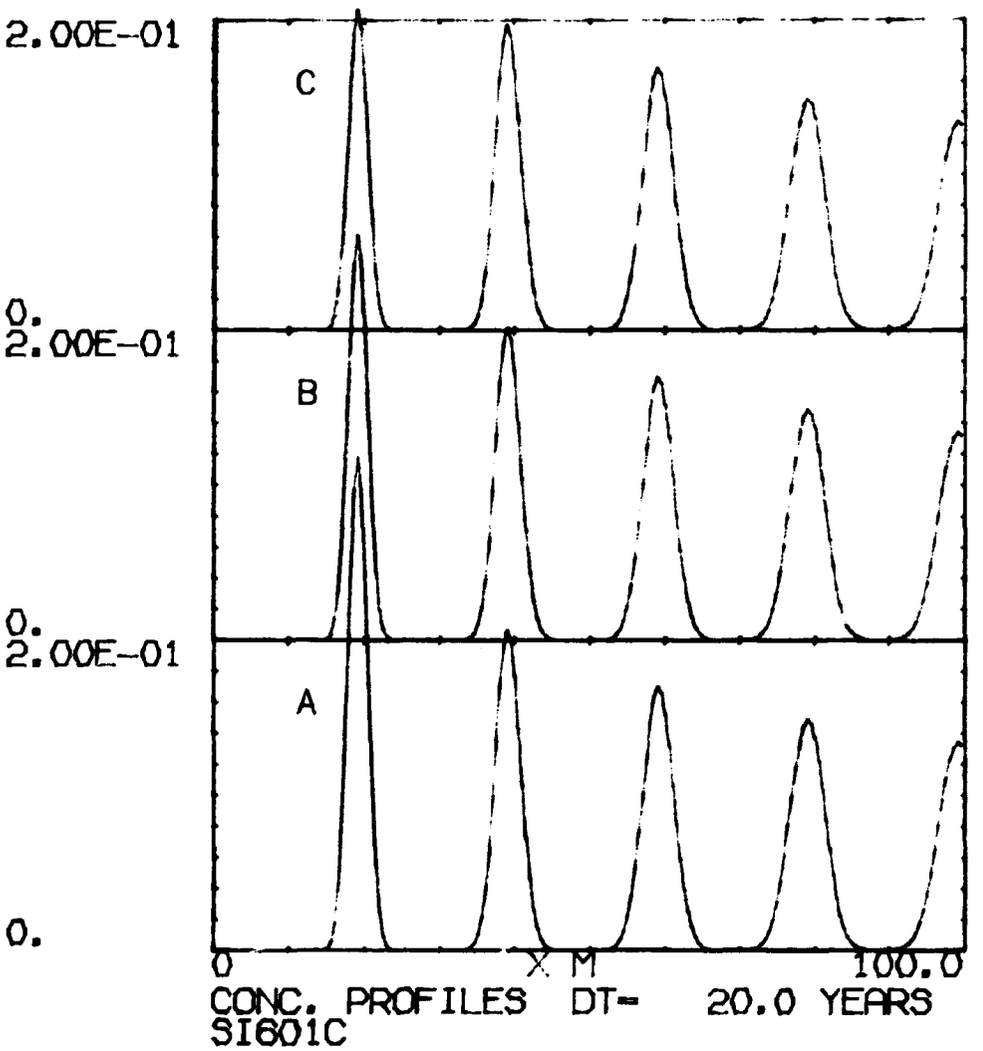

Figure 6-1. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}.

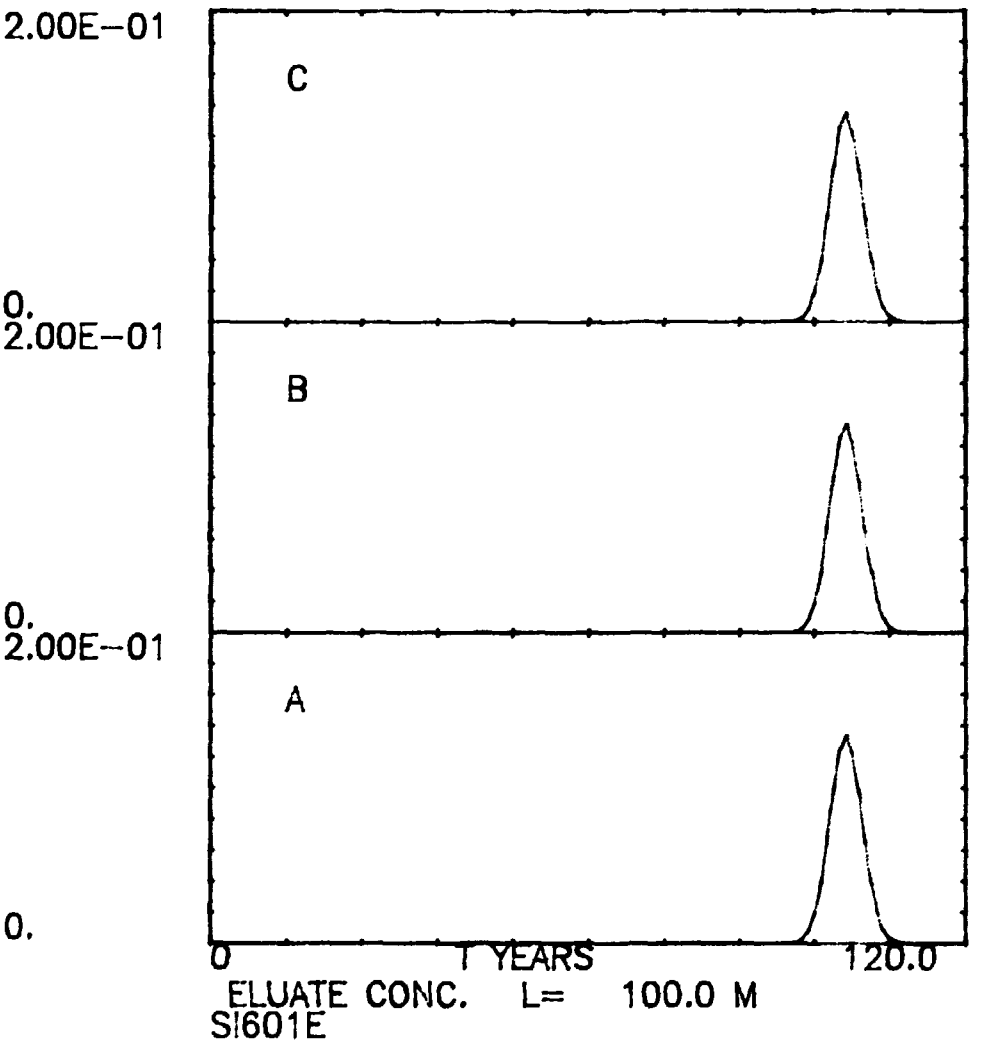

Figure 6-2. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}.

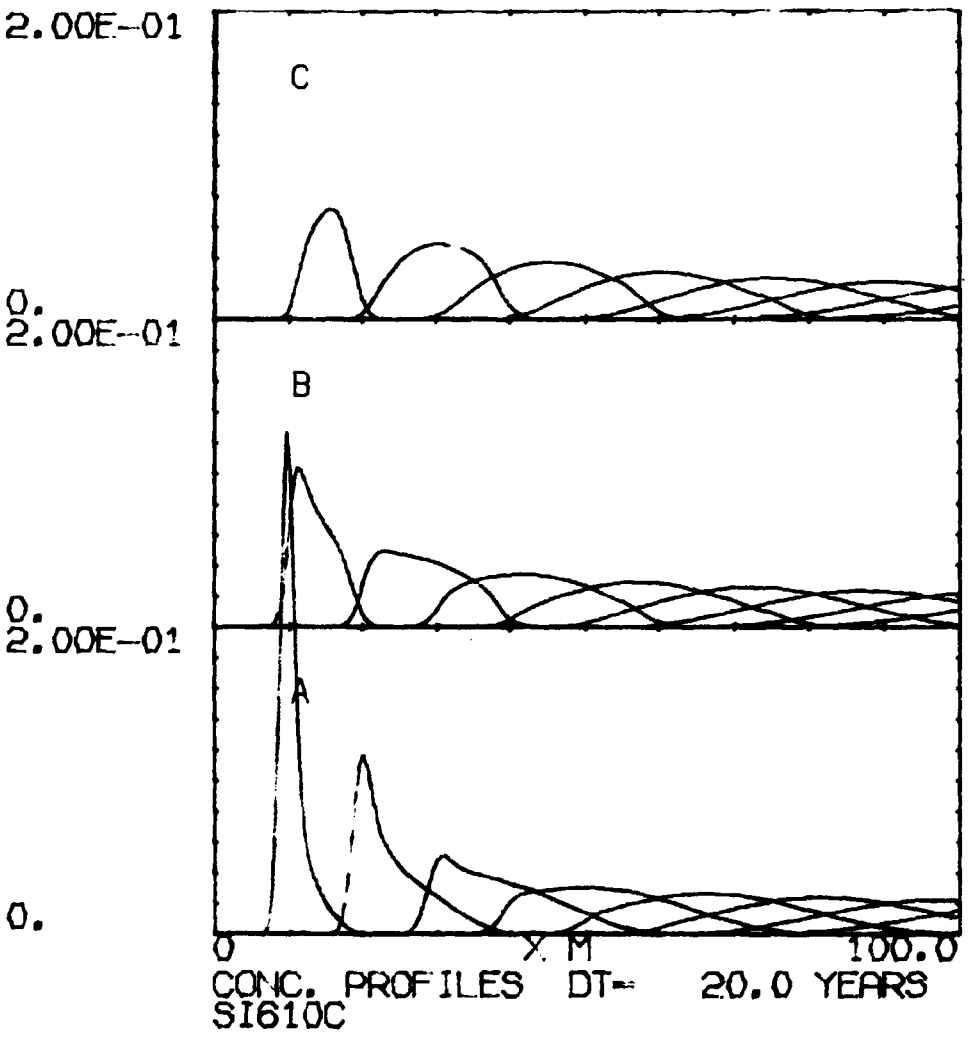

Figure 6-3. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}.

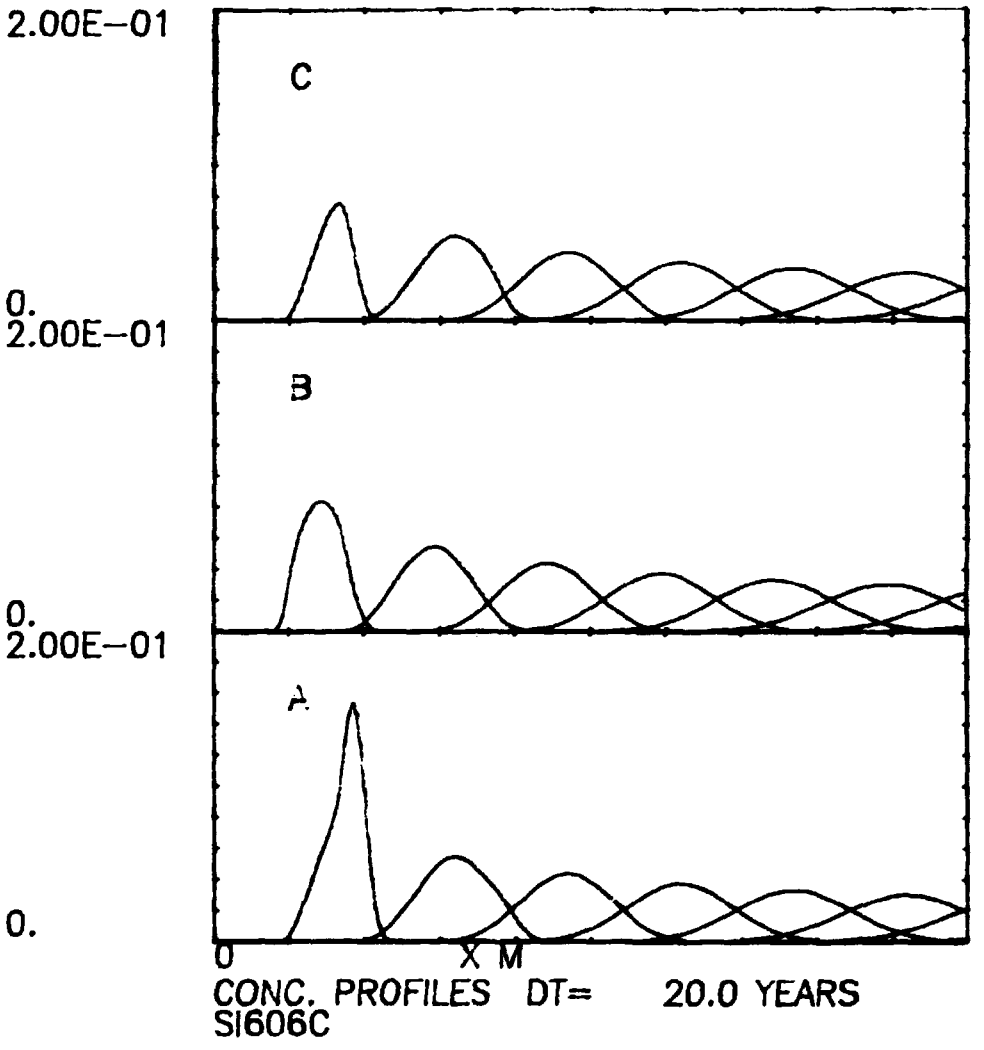

Figure 6-4. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}.

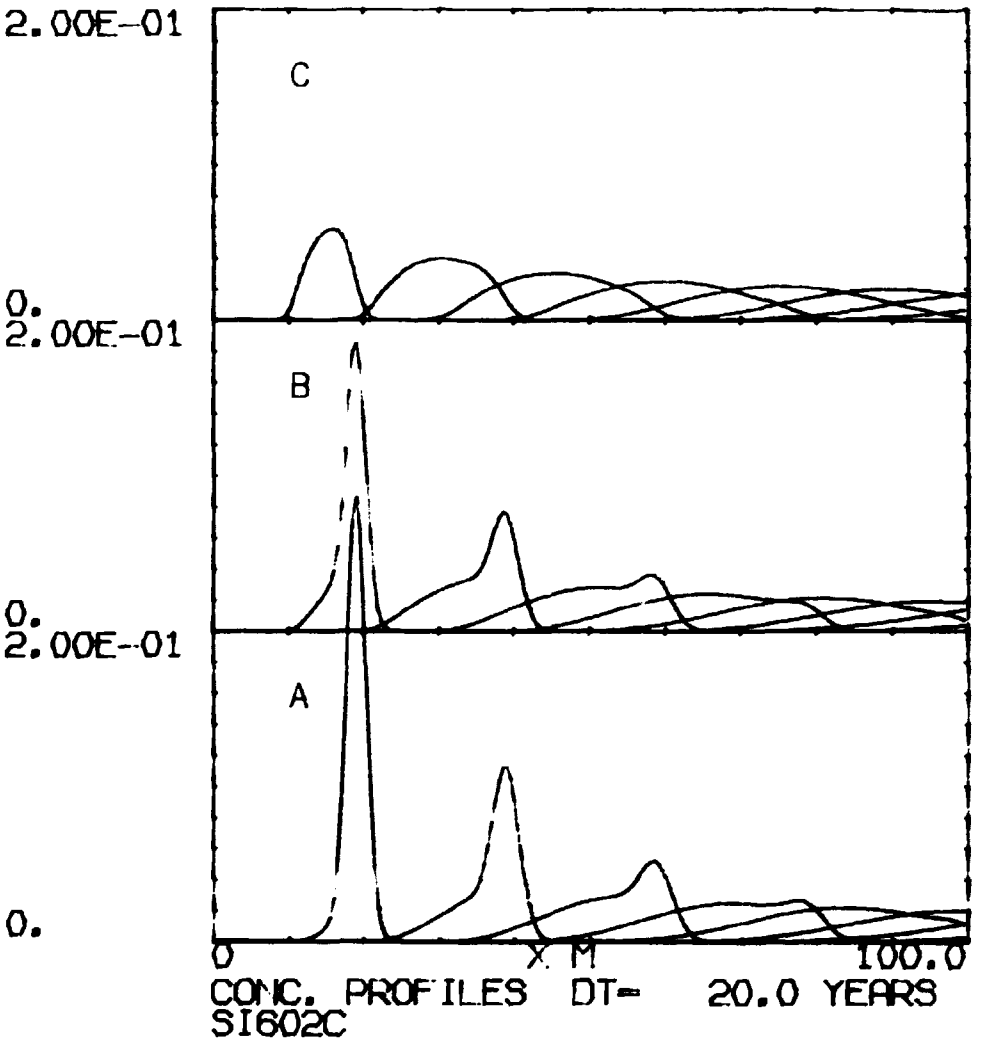

Figure 6-5. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}.

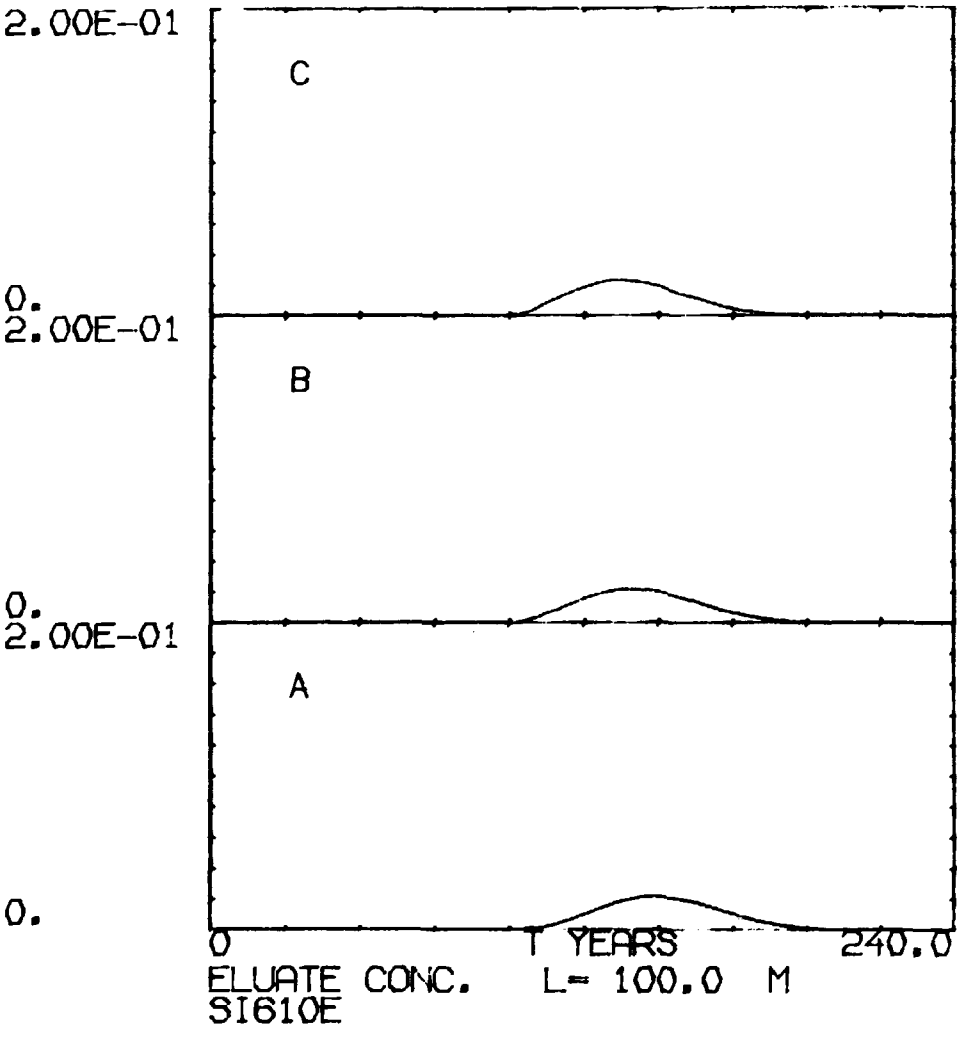

Figure 6-6. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}.

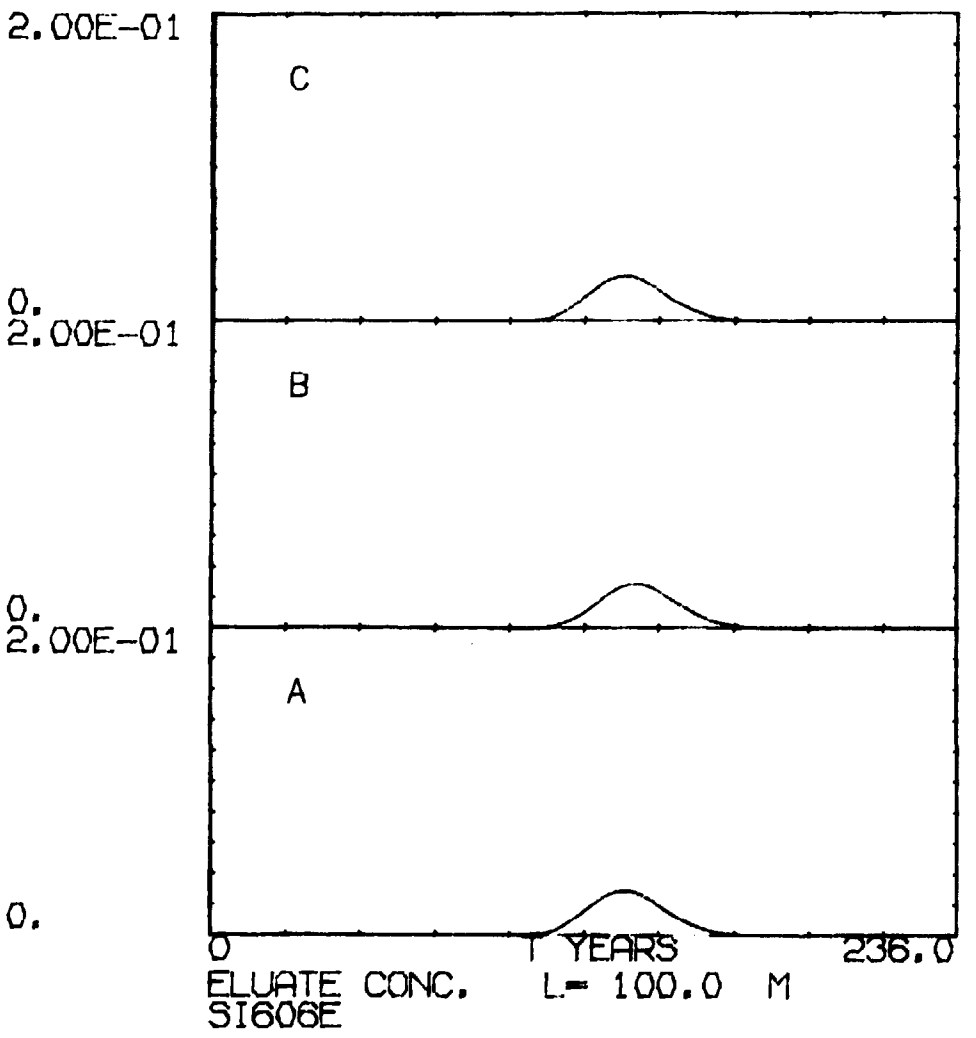

Figure 6-7. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}.

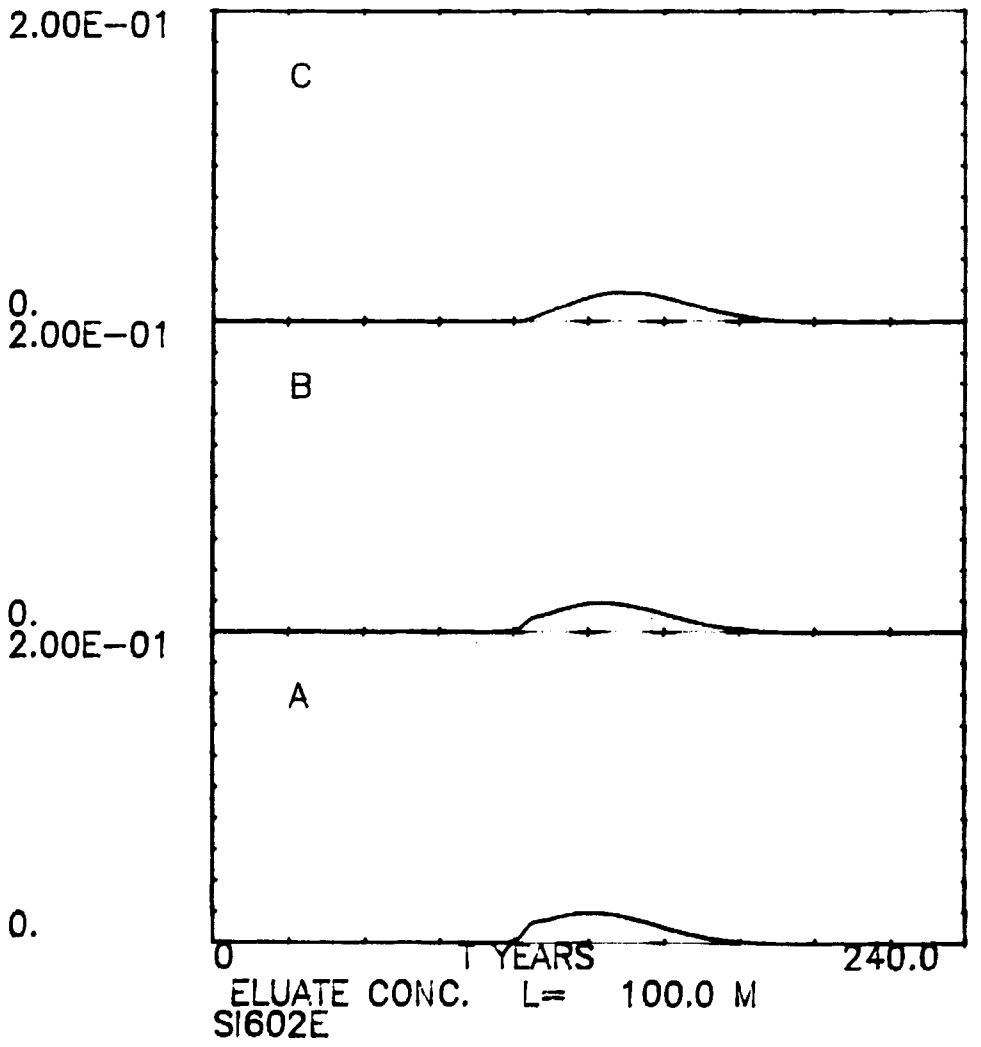

Figure 6-8. $R_{f(A)}=R_f(B)=1$, $R_f(C)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}.

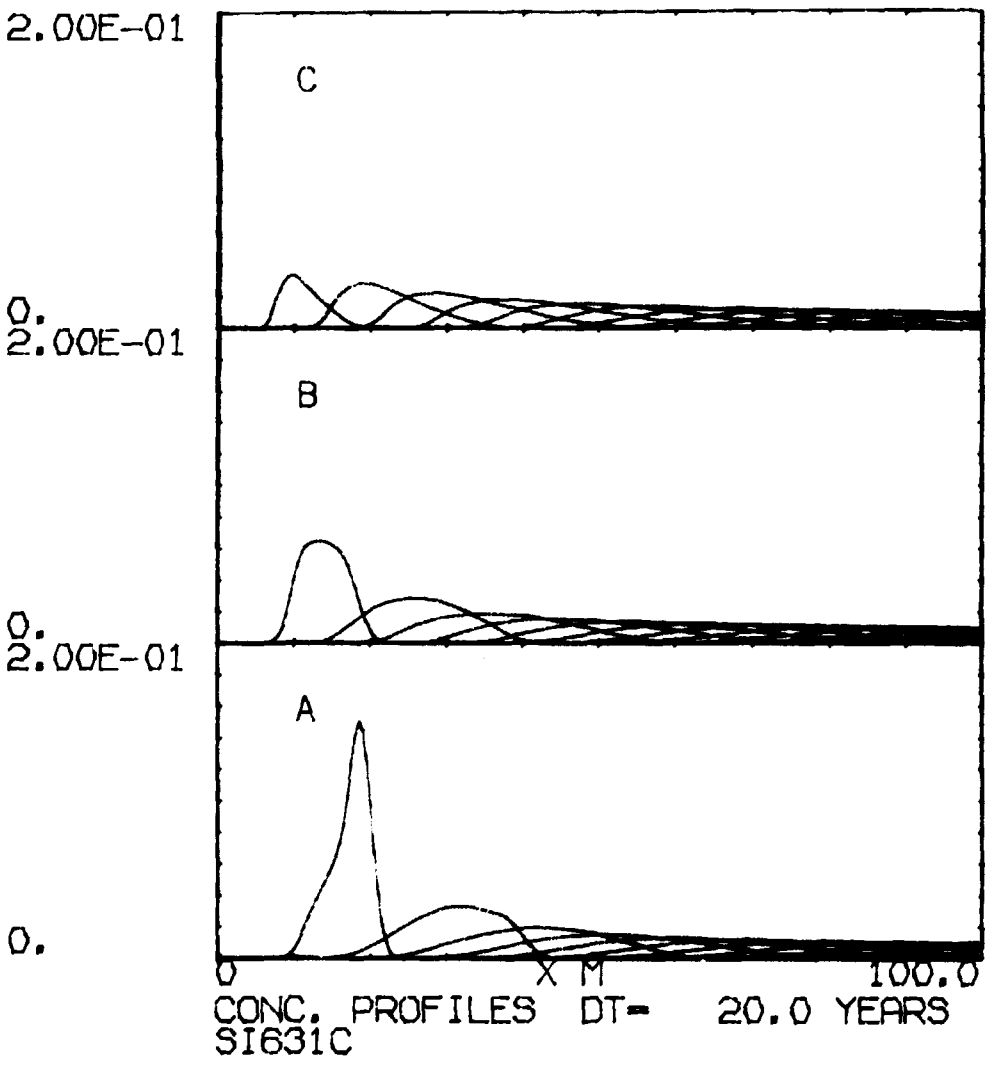

Figure 6-9. $R_f(A)=1$, $R_f(B)=2$, $R_f(C)=3$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}.

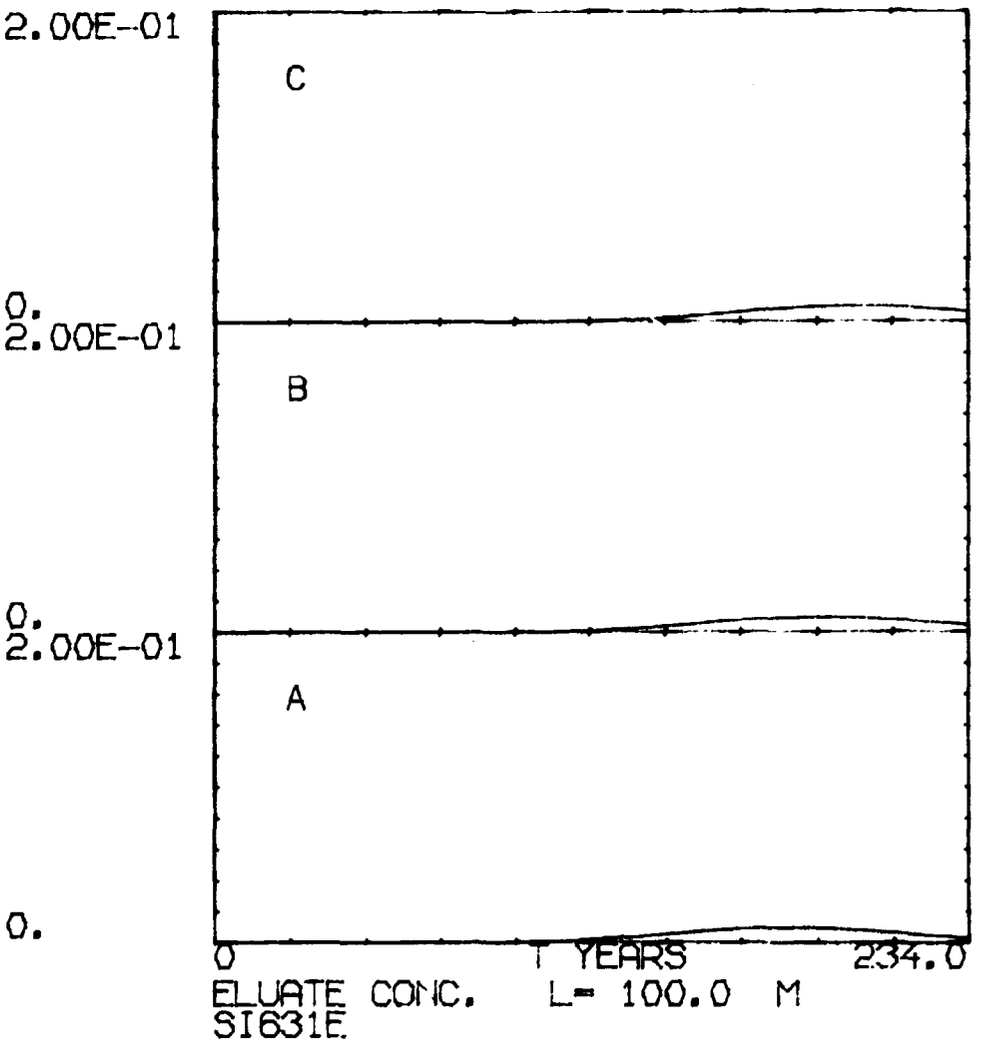

Figure 6-10. $R_f(A)=1$, $R_f(B)=2$, $R_f(C)=3$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.1$ y^{-1}.

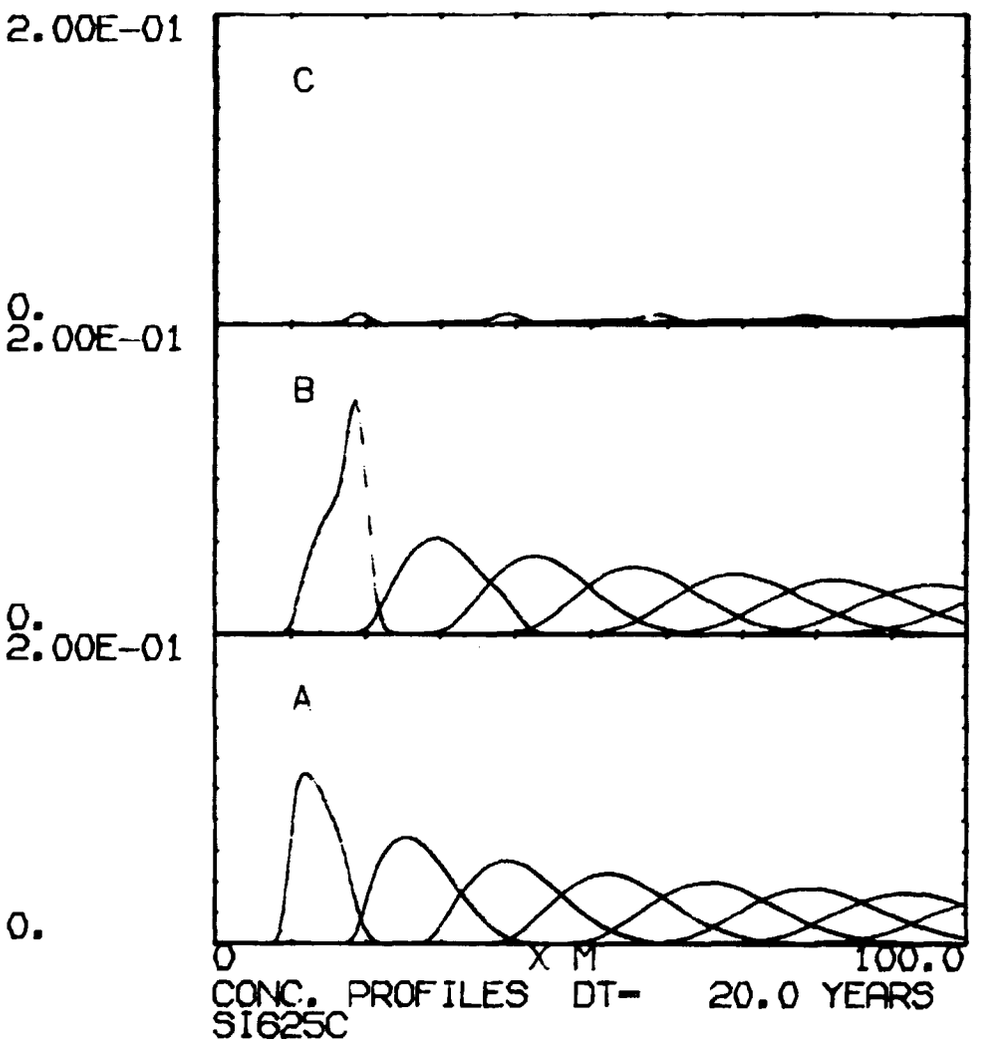

Figure 6-11. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}, $k_2=k_{-2}=0.001$ y^{-1}.

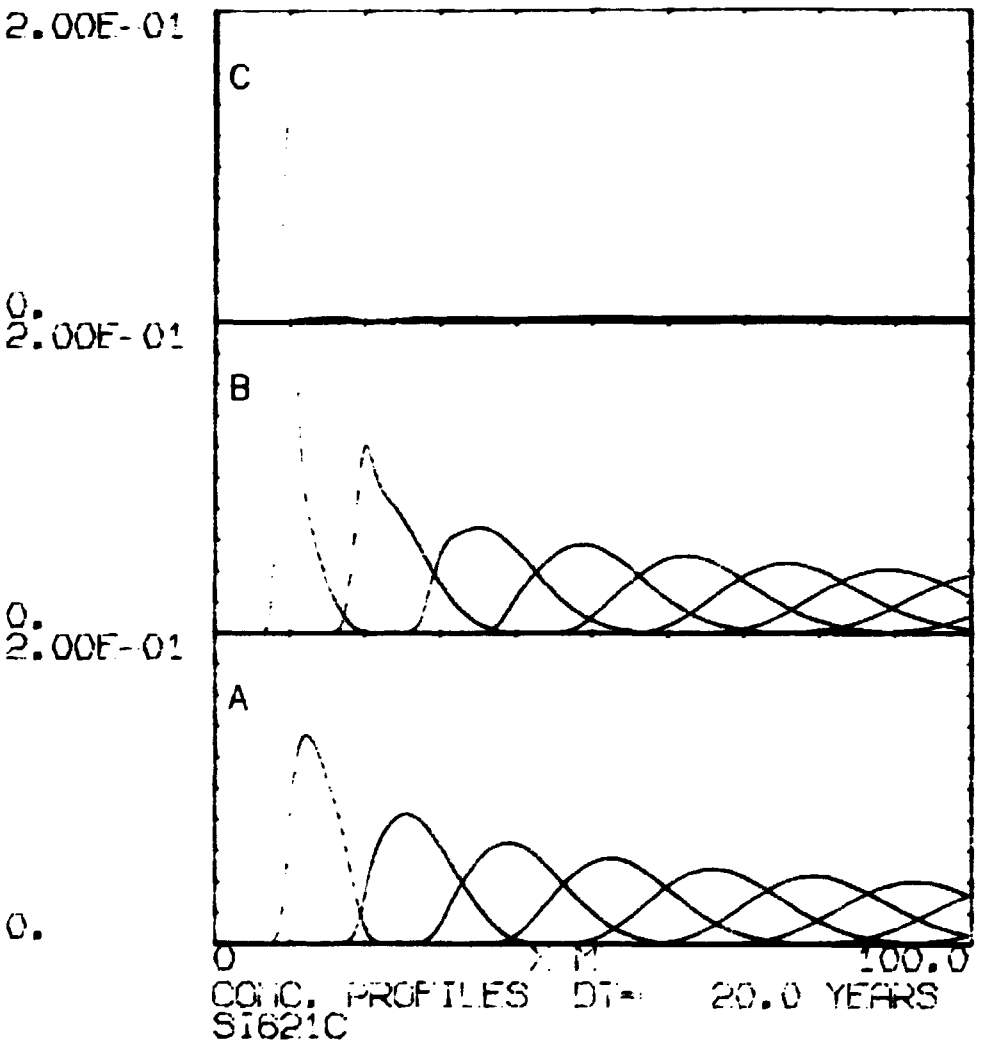

Figure 6-12. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}, $k_2=k_{-2}=0.001$ y^{-1}.

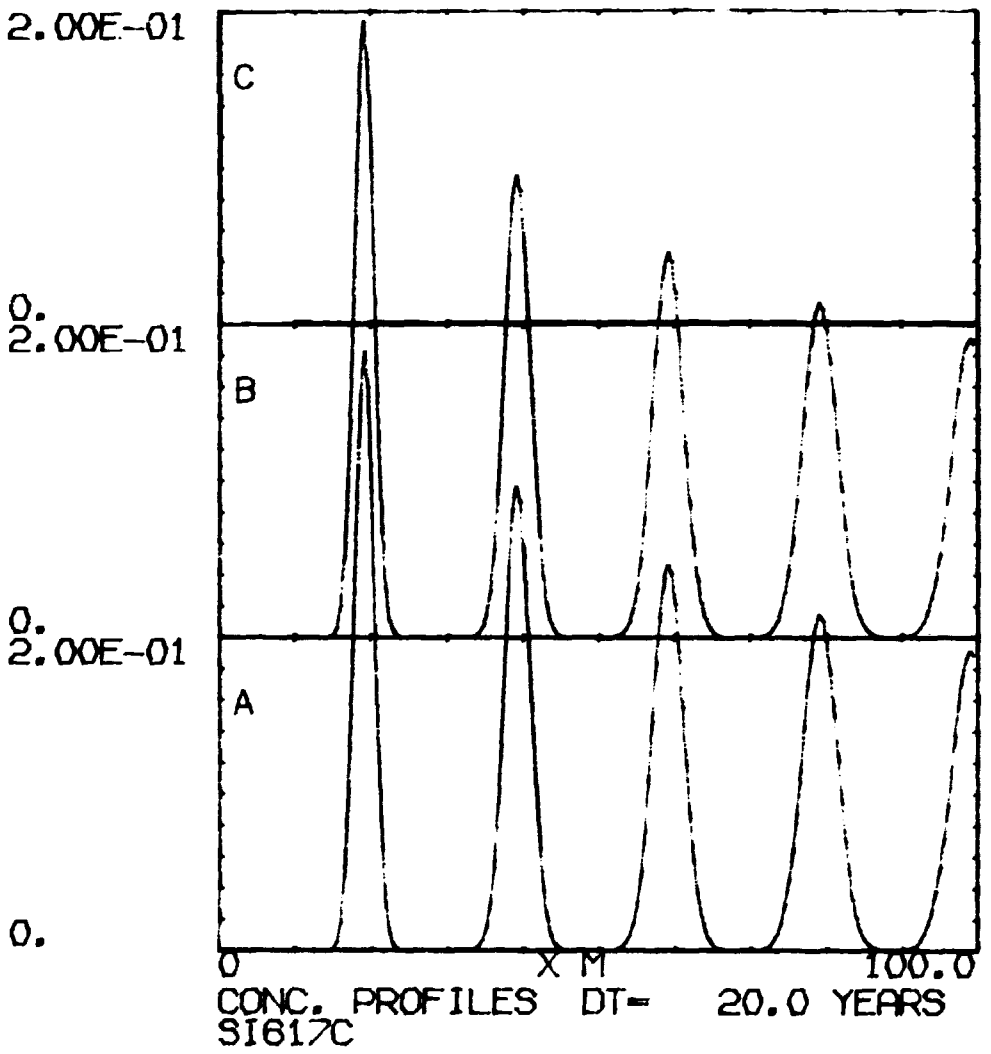

Figure 6-13. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}, $k_2=k_{-2}=0.001$ y^{-1}.

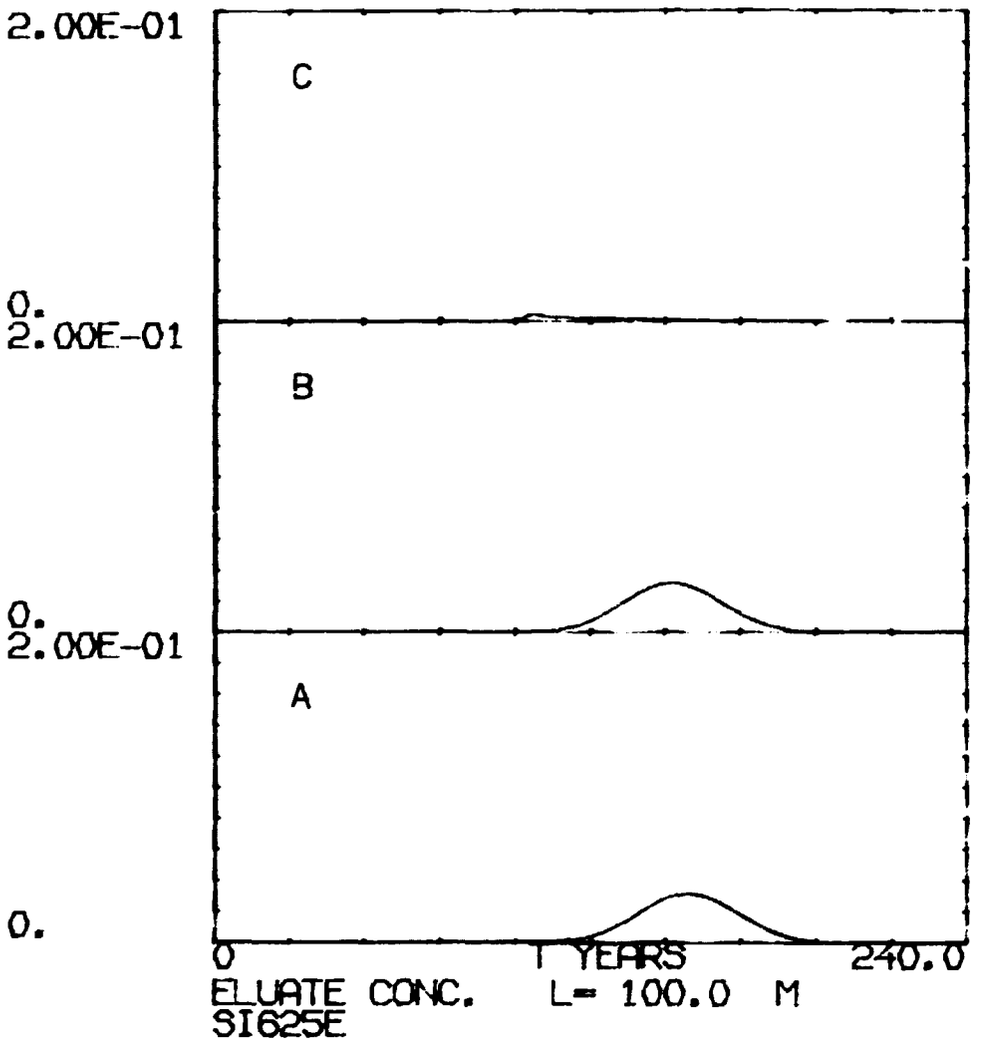

Figure 6-14. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}, $k_2=k_{-2}=0.001$ y^{-1}.

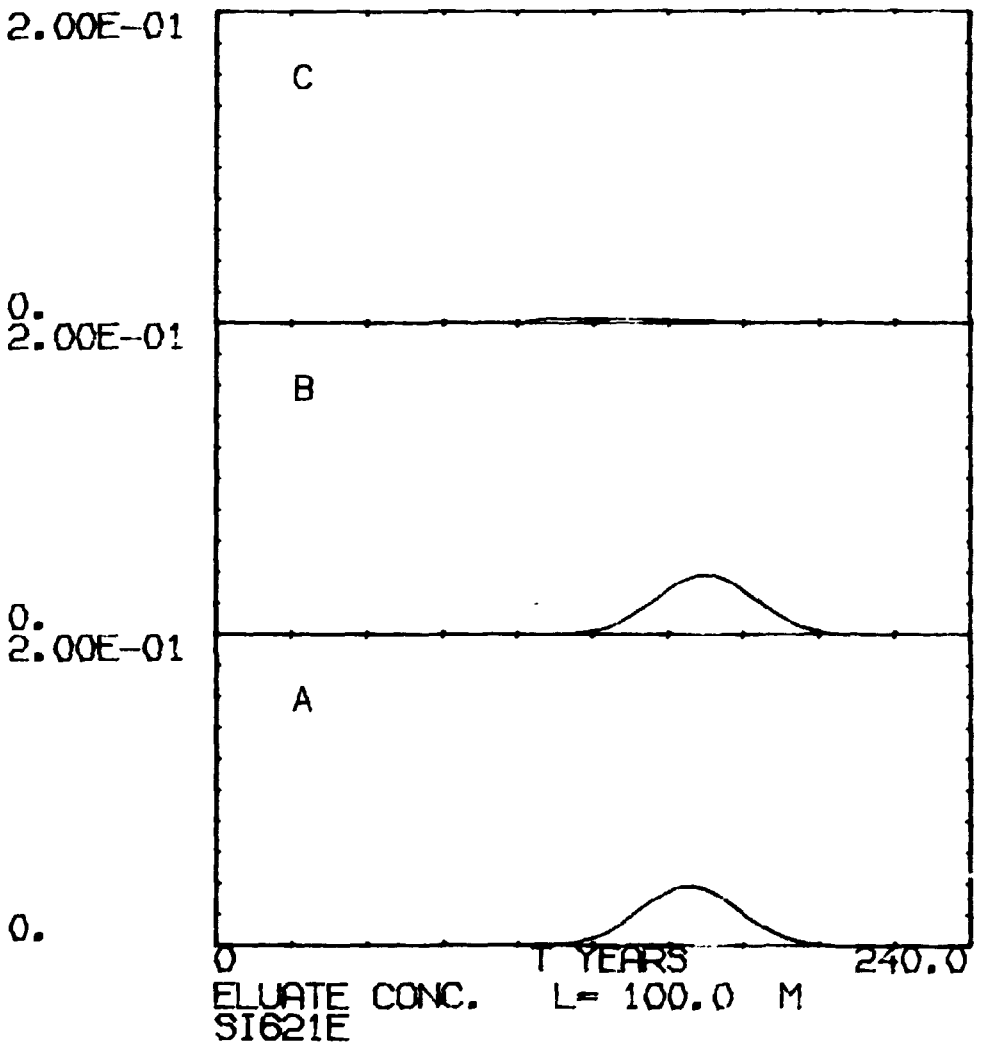

Figure 6-15. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}, $k_2=k_{-2}=0.001$ y^{-1}.

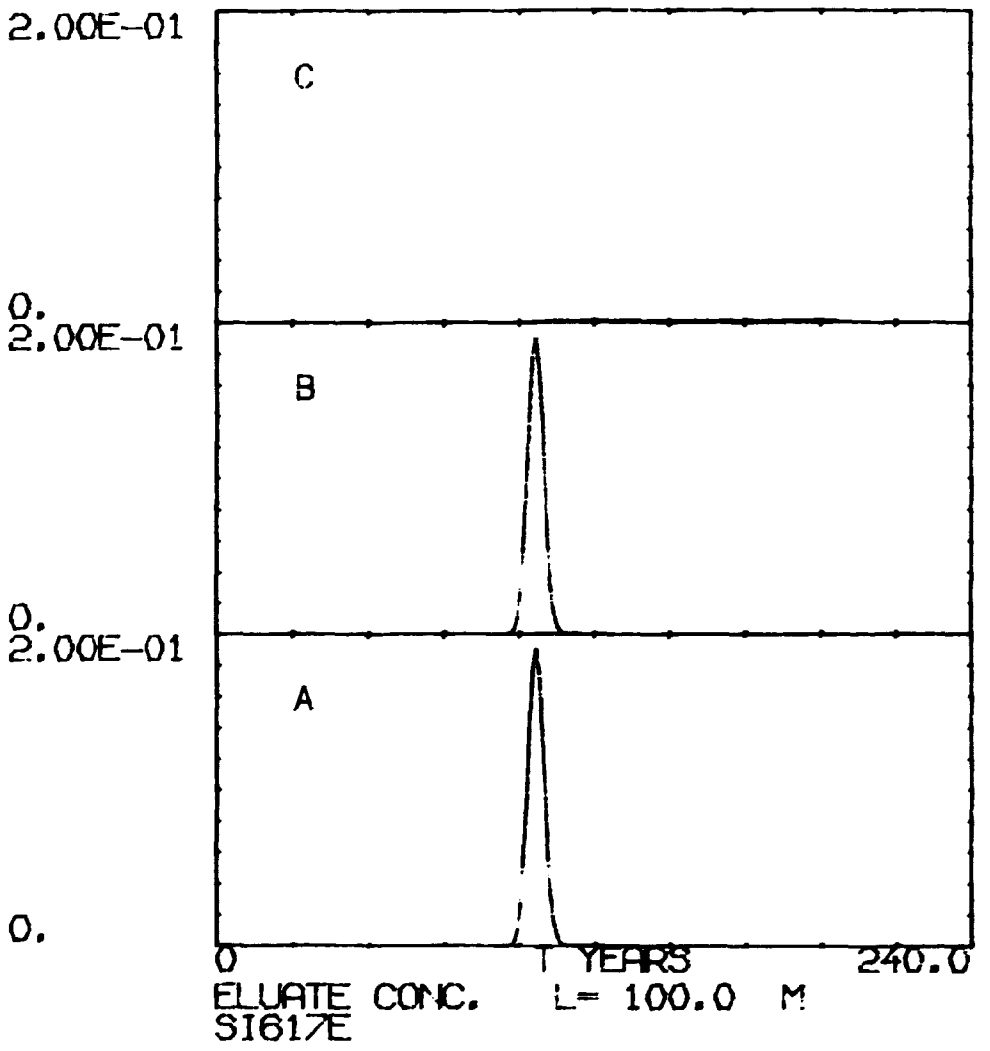

Figure 6-16. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}, $k_2=k_{-2}=0.001$ y^{-1}.

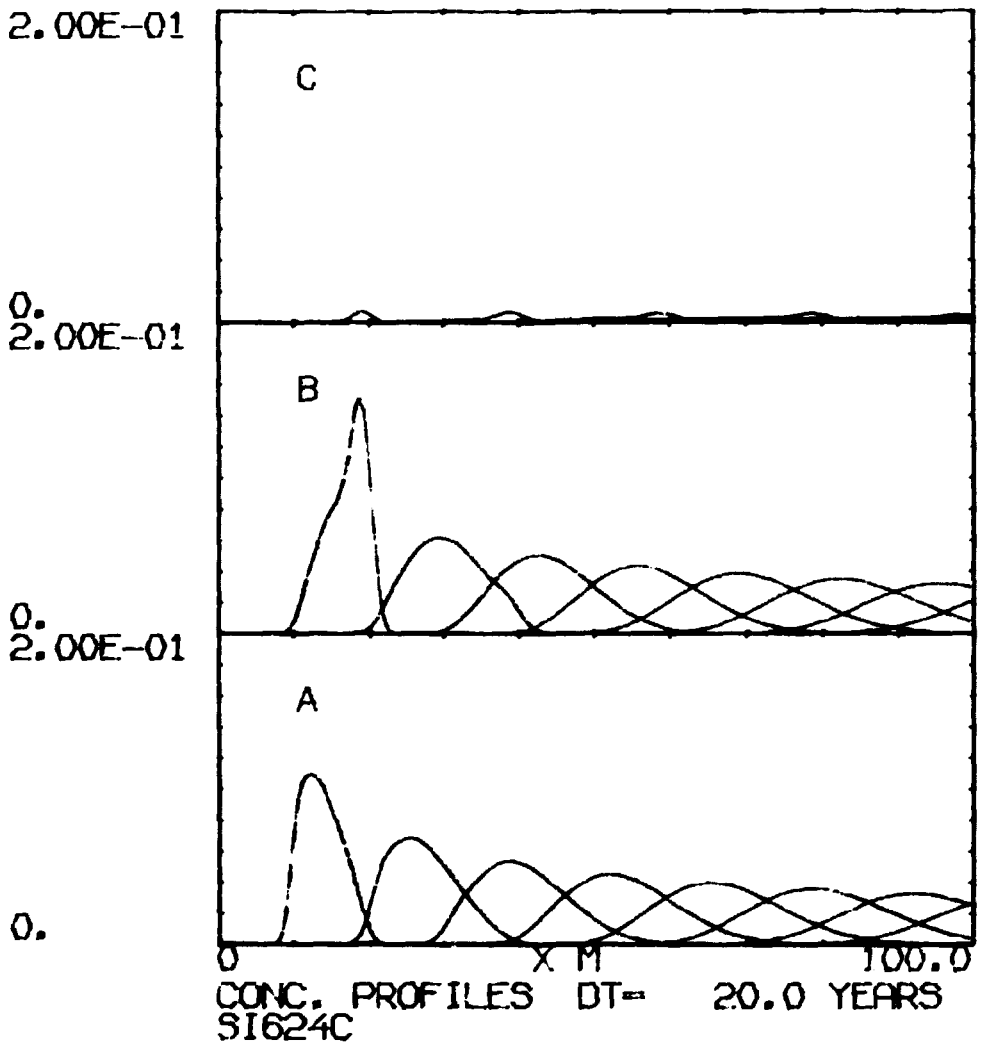

Figure 6-17. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}, $k_2=k_{-2}=0.01$ y^{-1}.

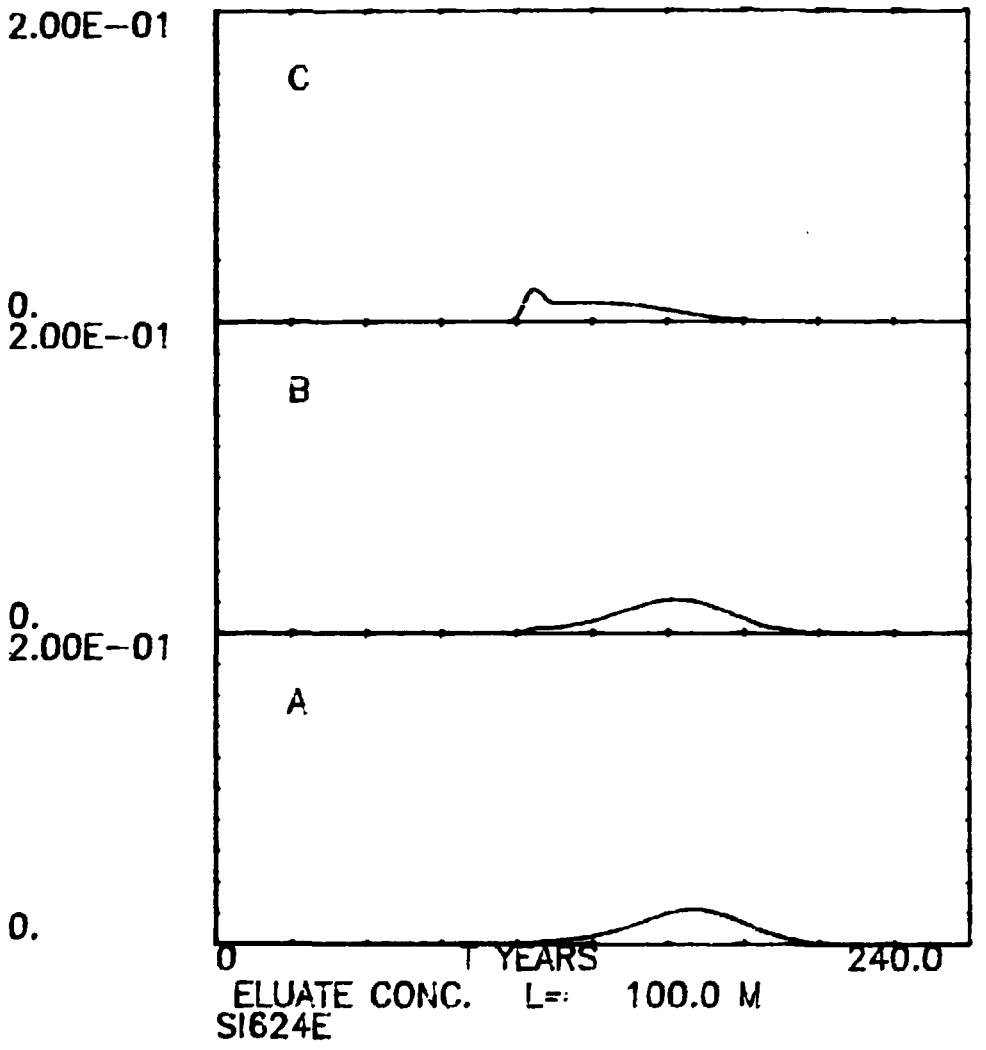

Figure 6-18. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ y^{-1}, $k_2=k_{-2}=0.01$ y^{-1}.

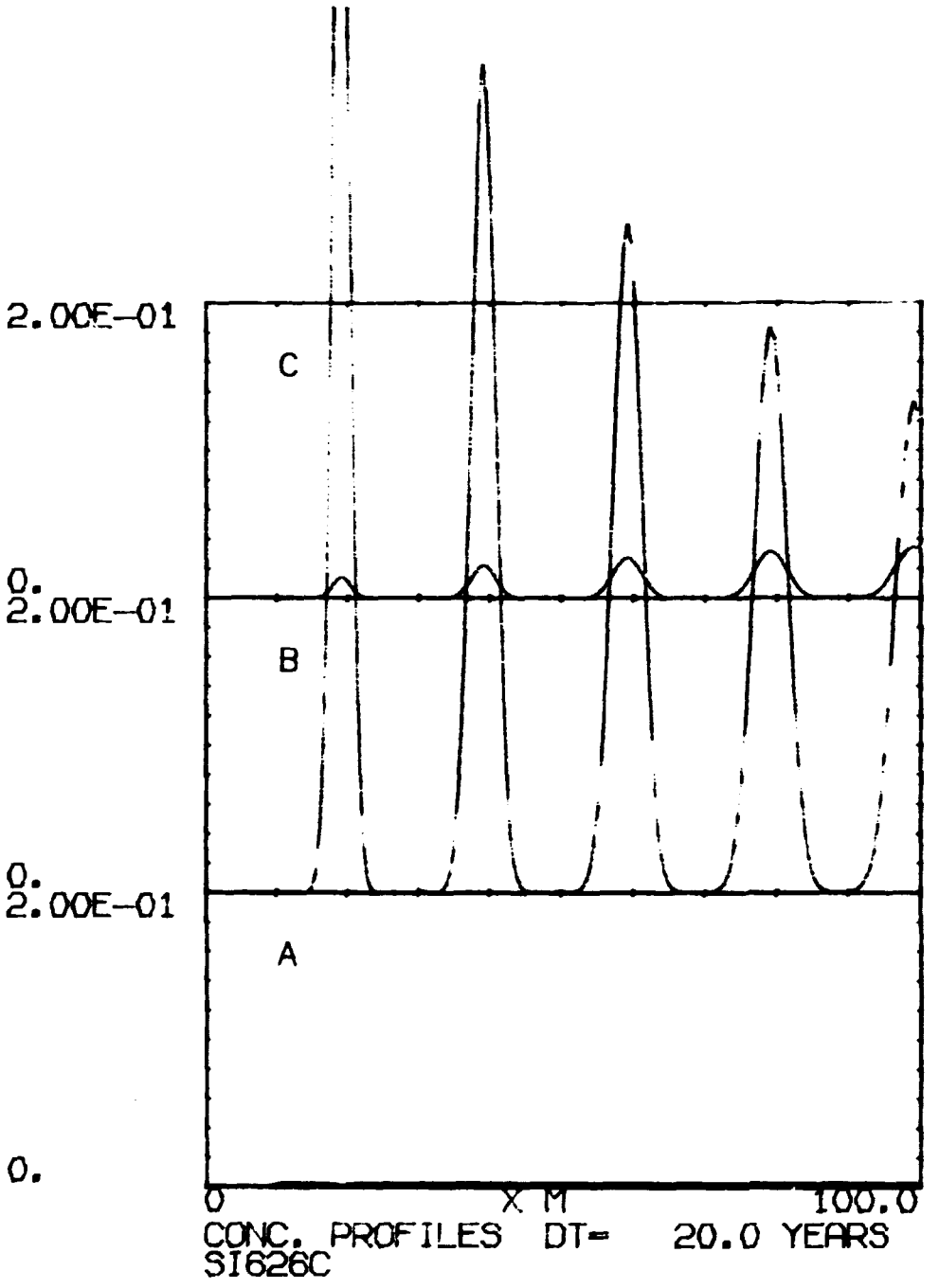

Figure 6-19. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.001$ y^{-1}.

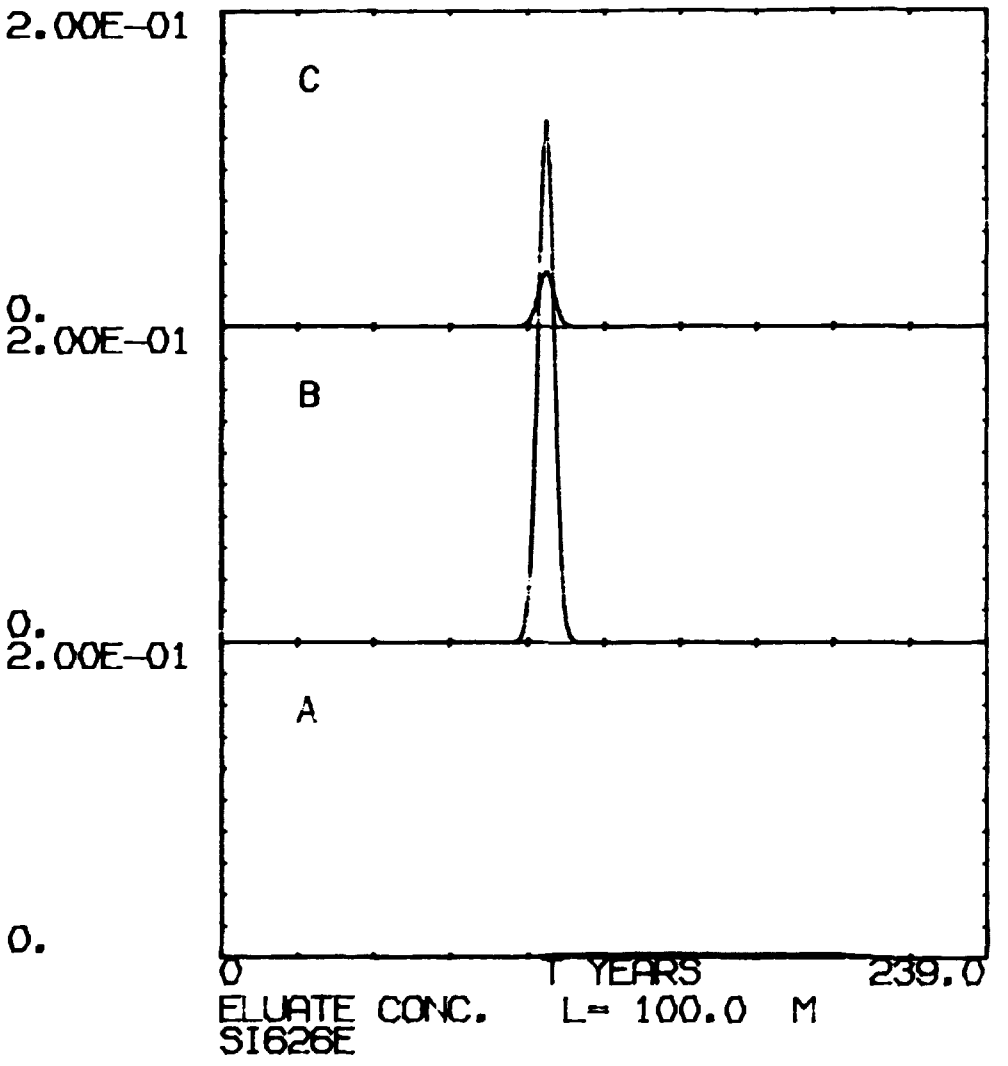

Figure 6-20. $R_f(A)=2$, $R_f(B)=R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.001$ y^{-1}.

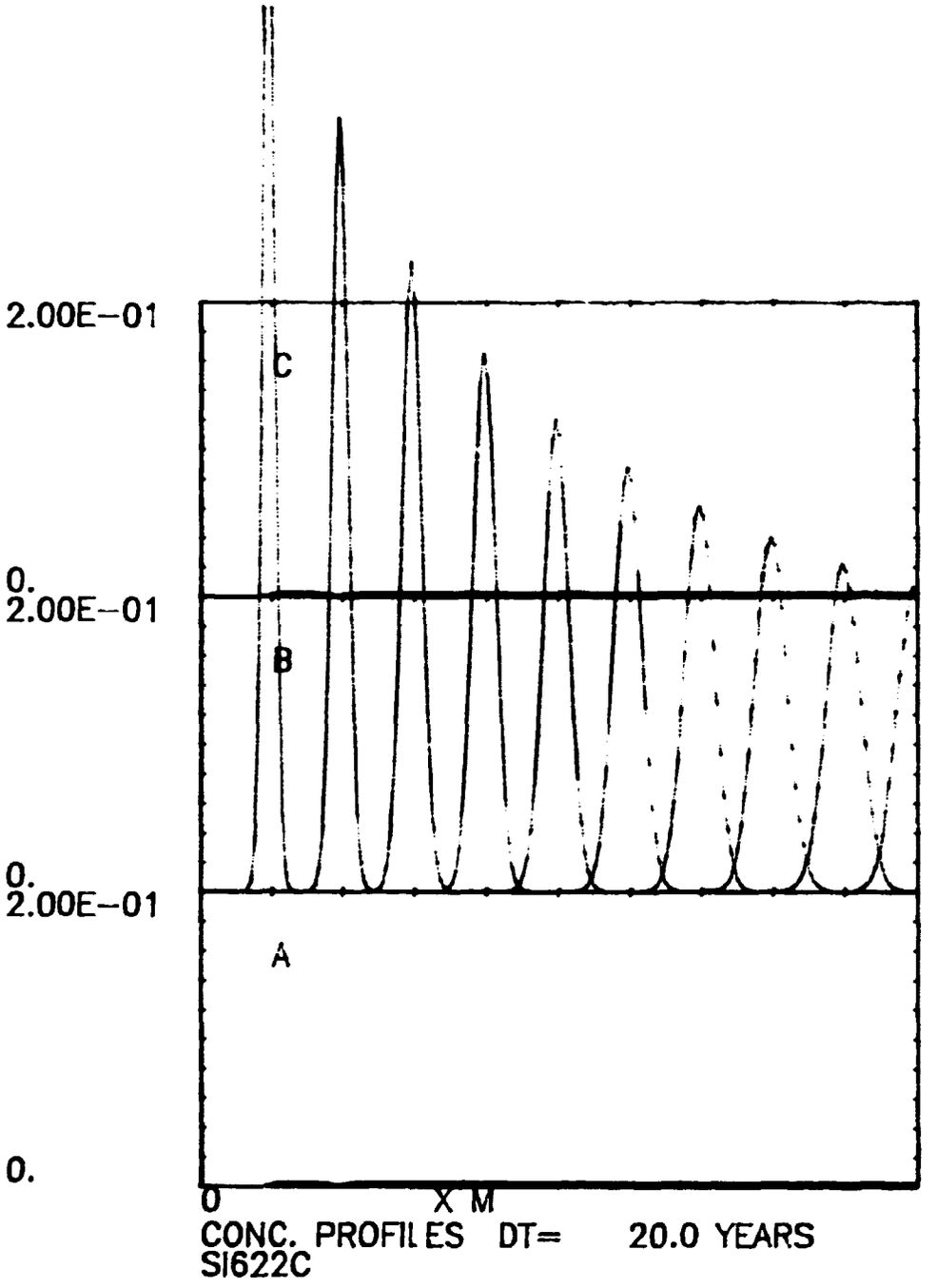

Figure 6-21. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.001$ y^{-1}.

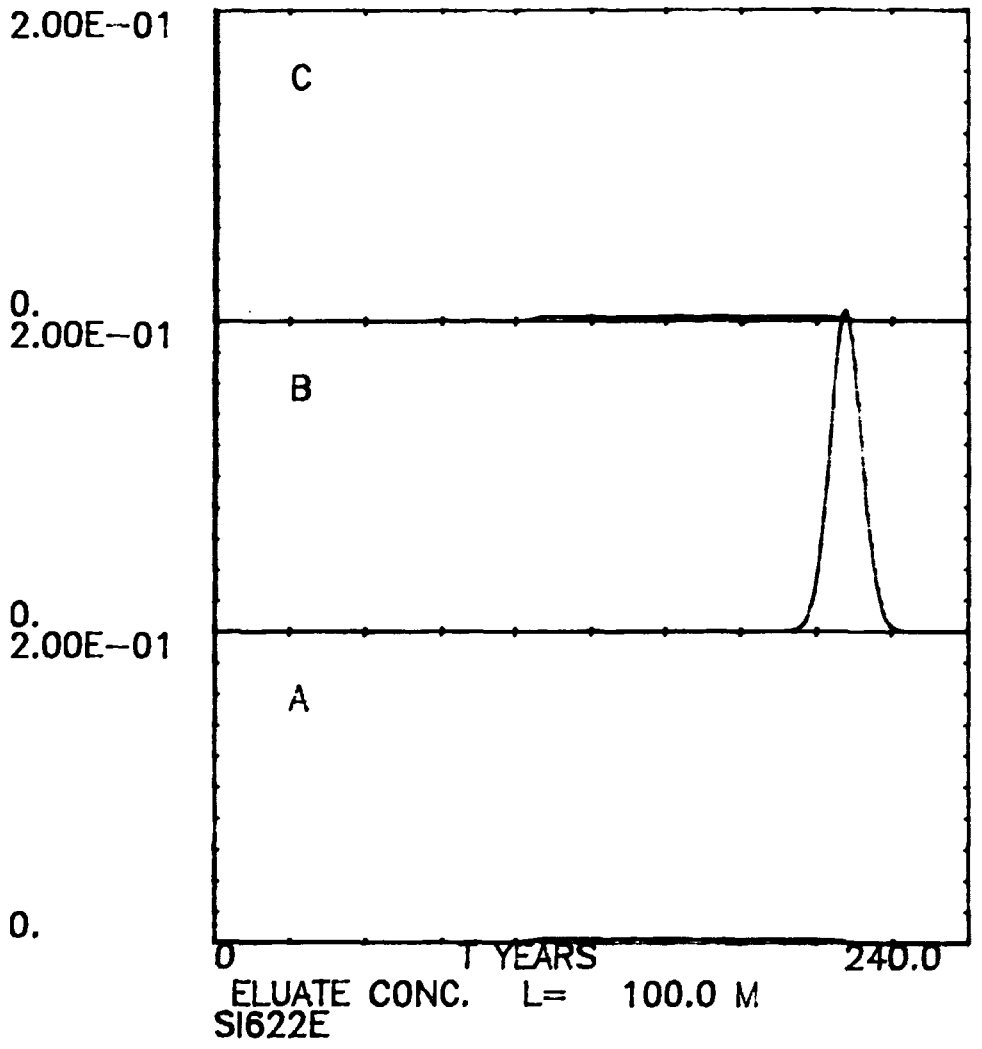

Figure 6-22. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=k_2=k_{-2}=0.001$ y^{-1}.

FIGURES FOR SECTION 4.7

$$A + X \rightarrow B$$

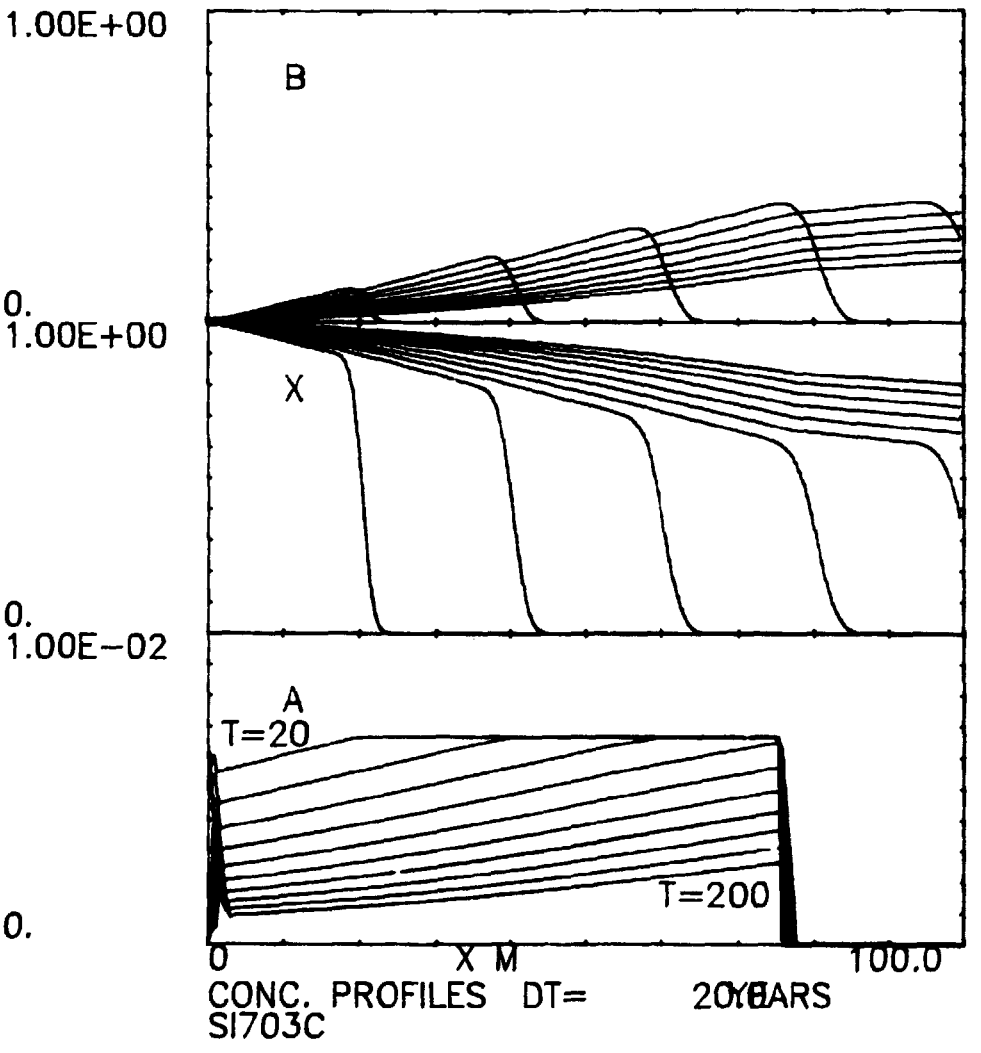

Figure 7-1. $R_f(A)=100$, $R_f(X)=R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$.

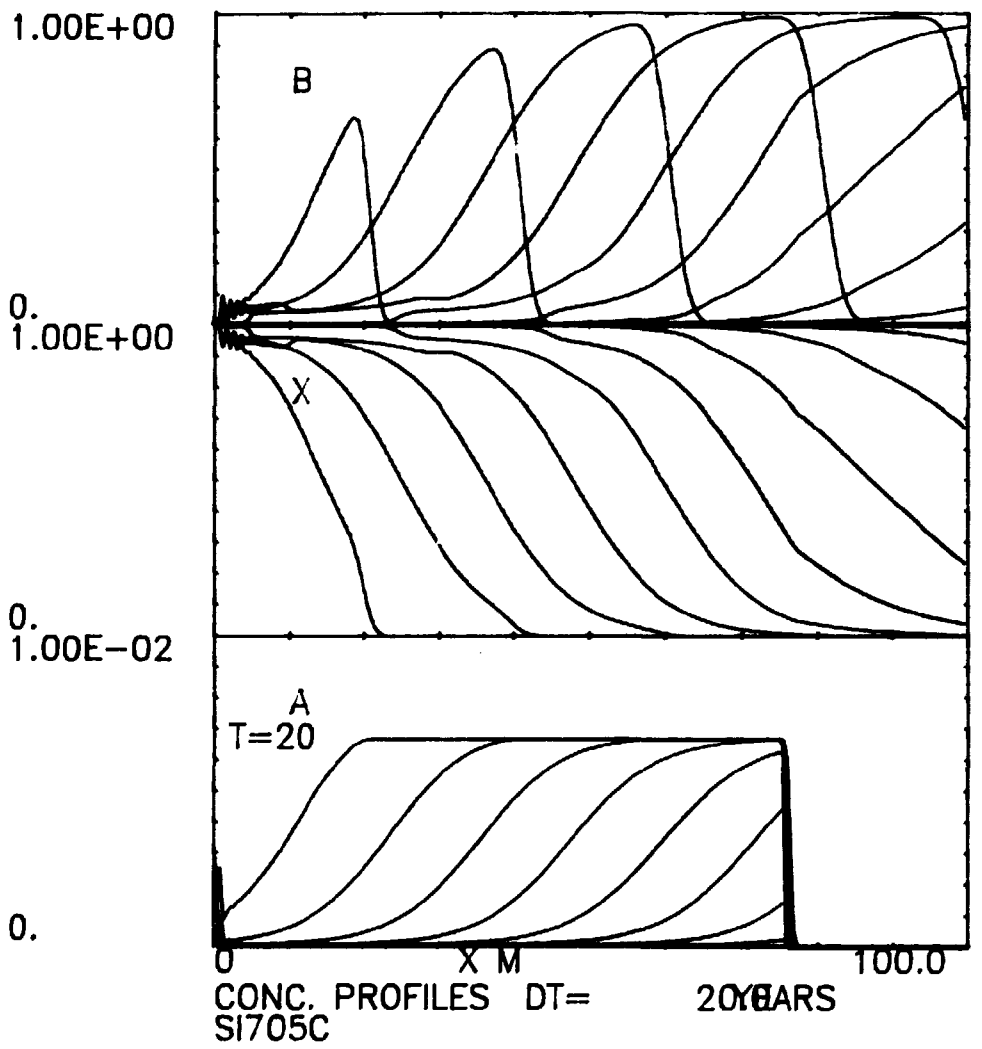

Figure 7-2. $R_f(A)=100$, $R_f(X)=R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=10$ $M^{-1}y^{-1}$.

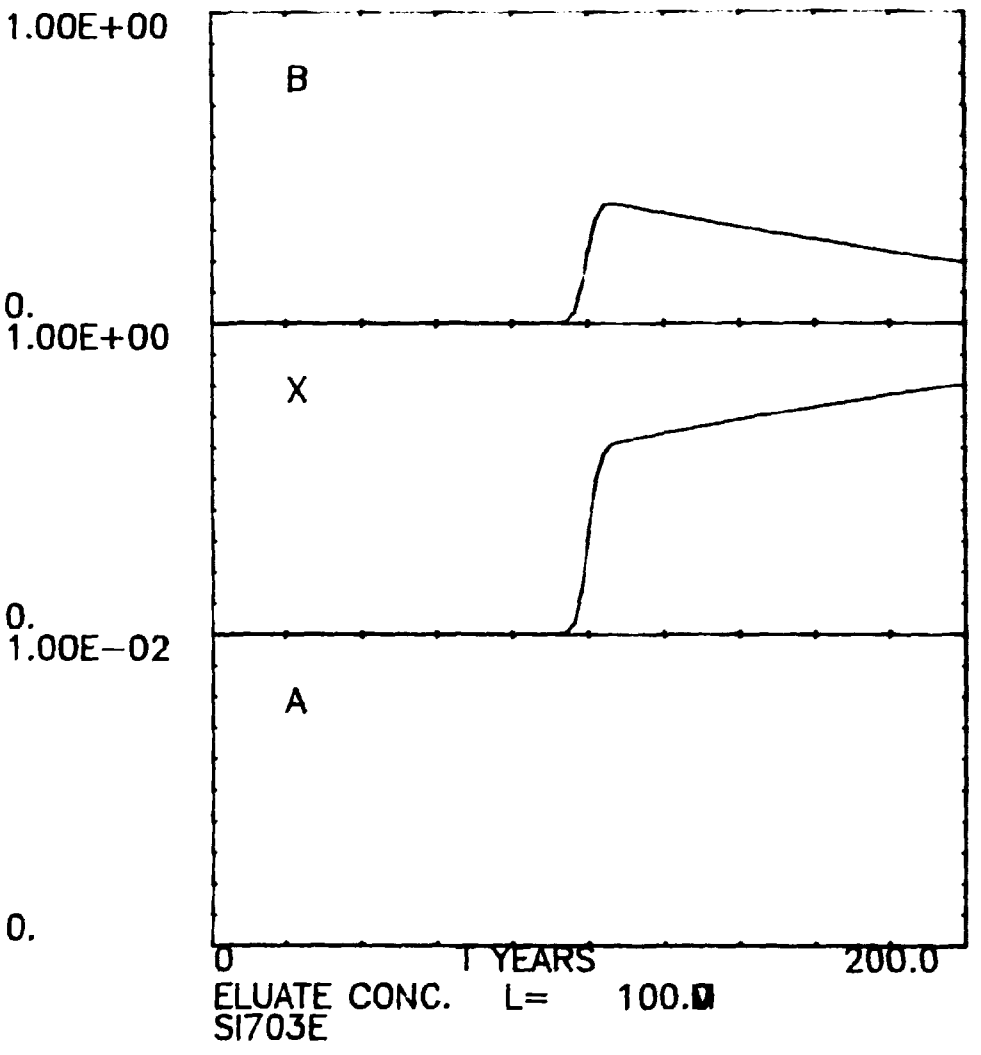

Figure 7-3. $R_f(A)=100$, $R_f(X)=R_f(B)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=1$ $M^{-1}y^{-1}$.

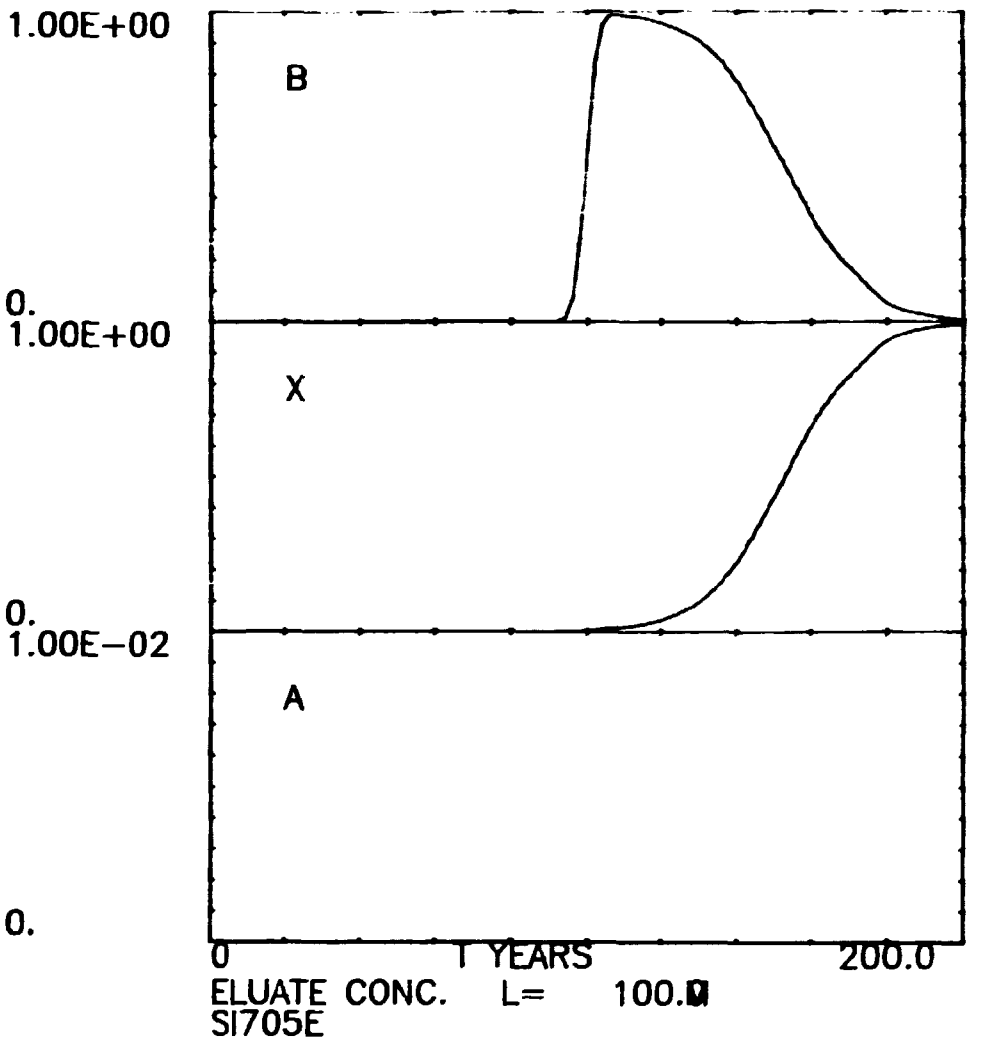

Figure 7-4. $R_f(A)=100$, $R_f(X)=R_f(B)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=10$ $M^{-1}y^{-1}$.

FIGURES FOR SECTION 4.8

$$A+B \rightleftarrows C$$

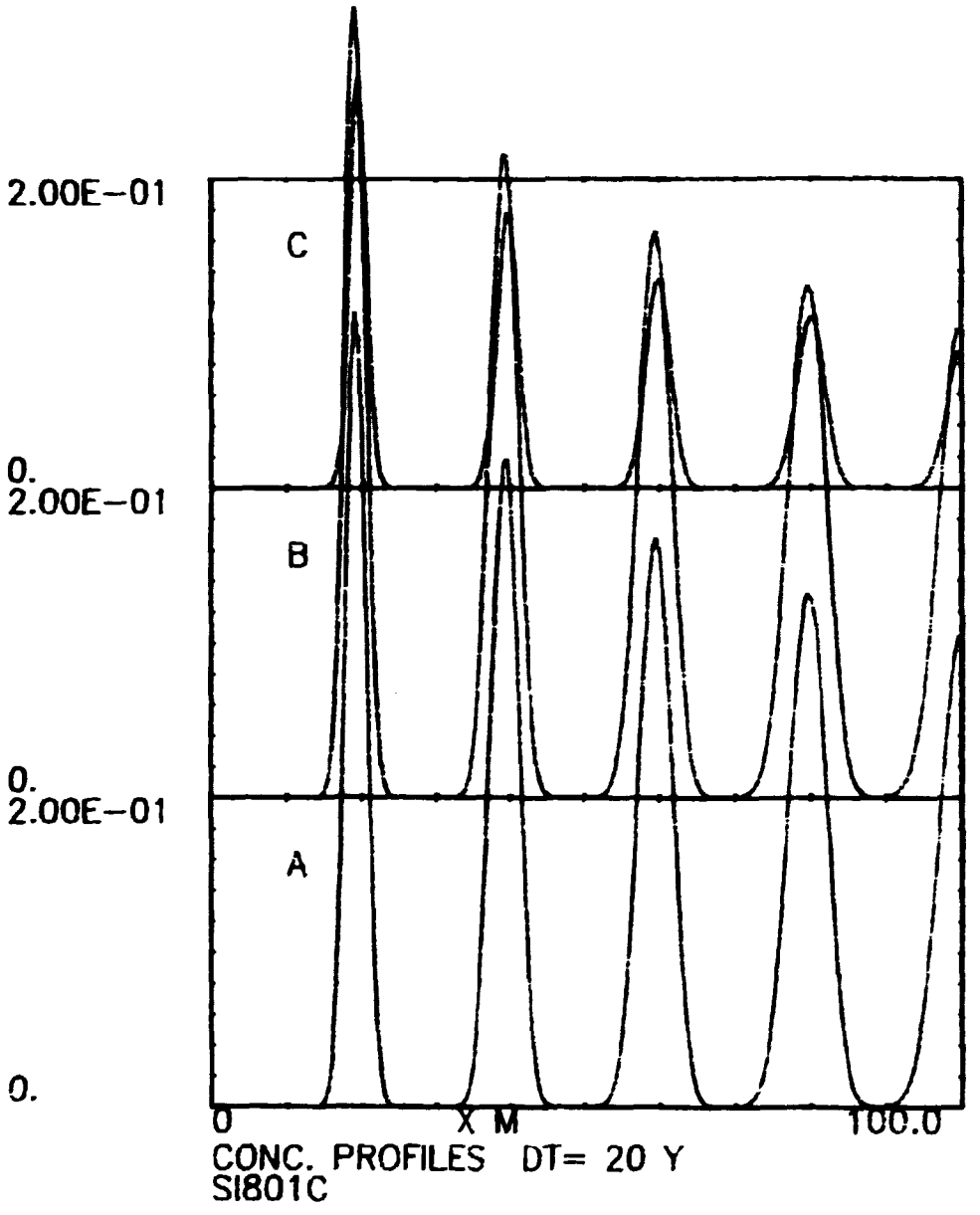

Figure 8-1. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-1}, $k_1=0.1\ M^{-1}y^{-1}$, $k_{-1}=0.1\ y^{-1}$.

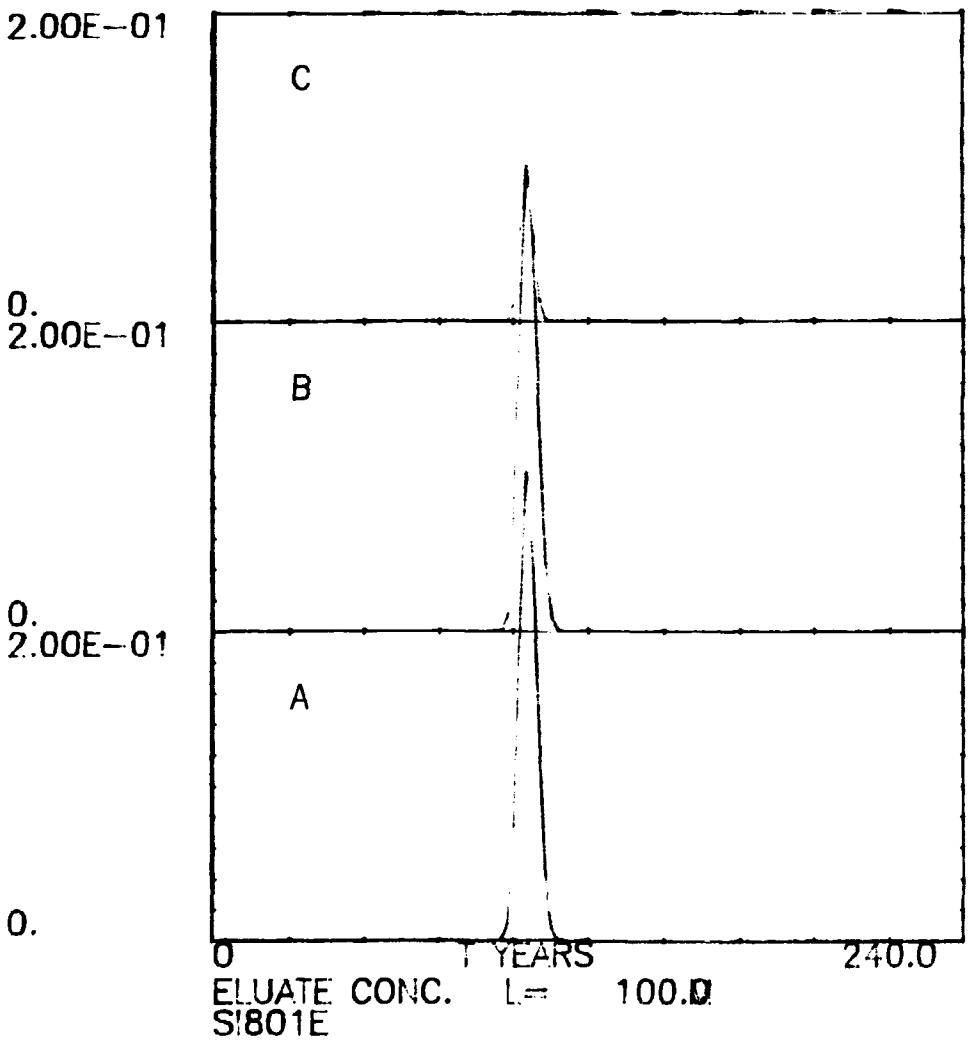

Figure 8-2. $R_f(A)=R_f(B)=R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1\ M^{-1}y^{-1}$, $k_{-1}=0.1\ y^{-1}$.

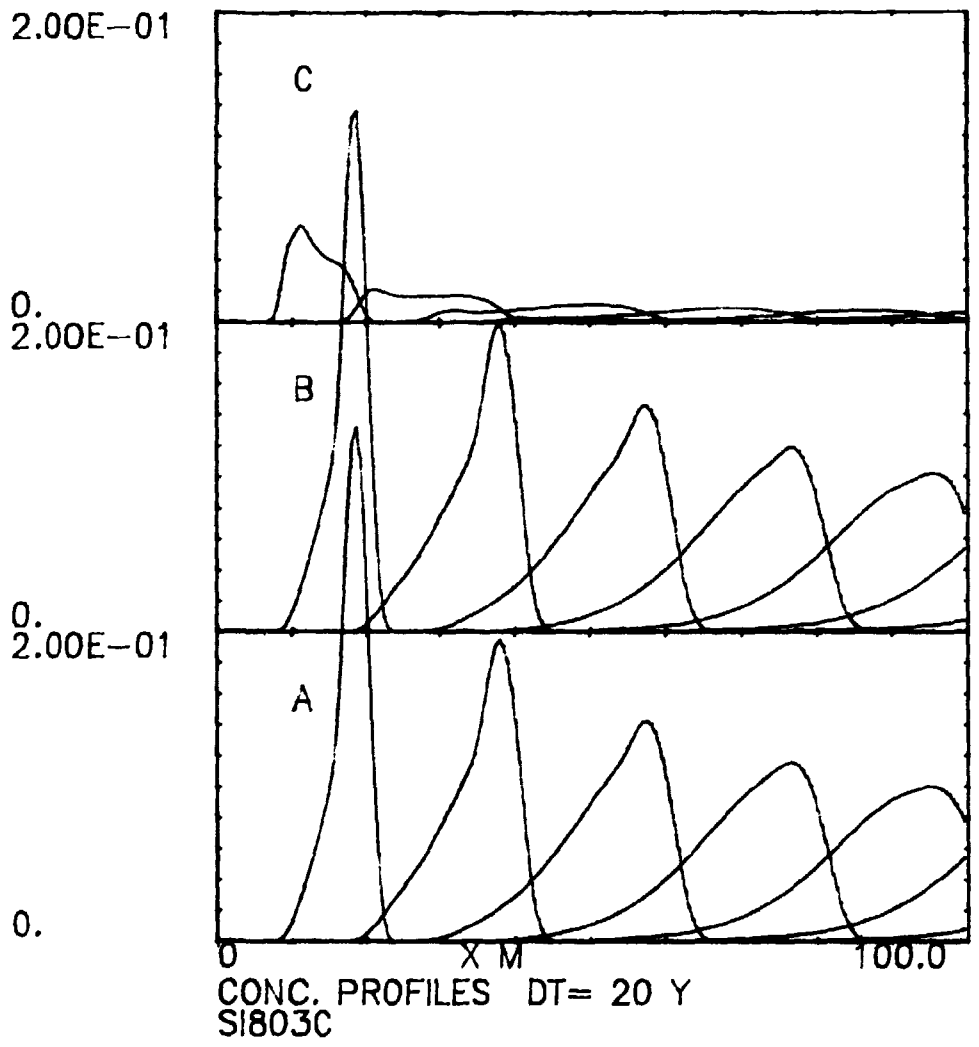

Figure 8-3. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.1$ y^{-1}.

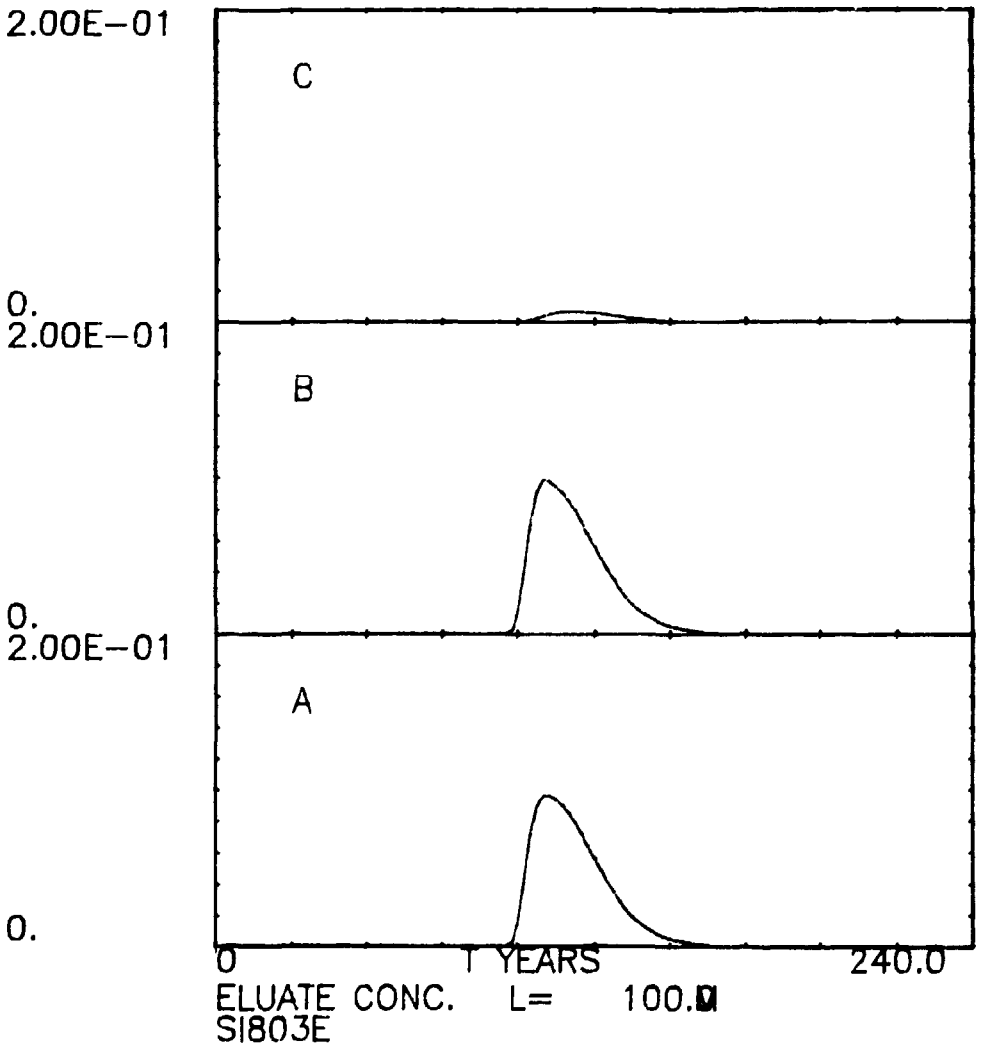

Figure 8-4. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.1$ y^{-1}.

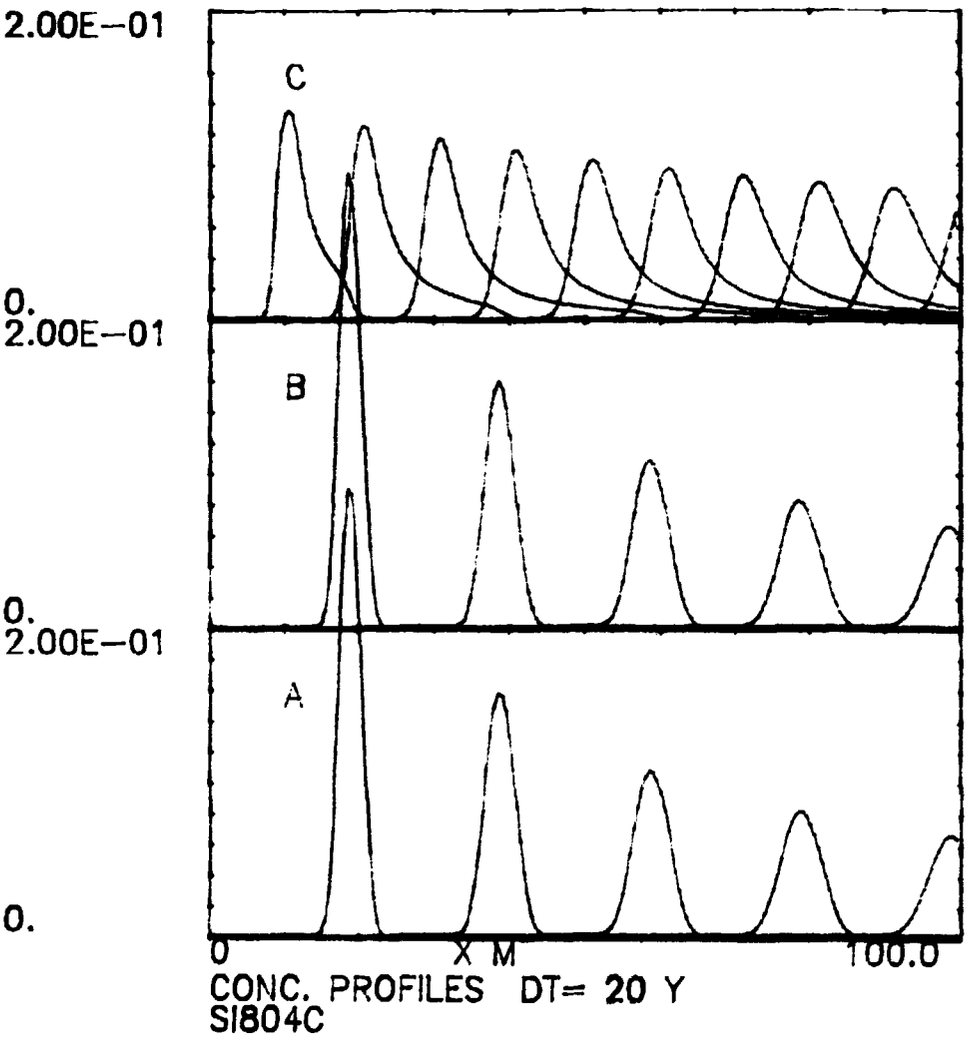

Figure 8-5. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

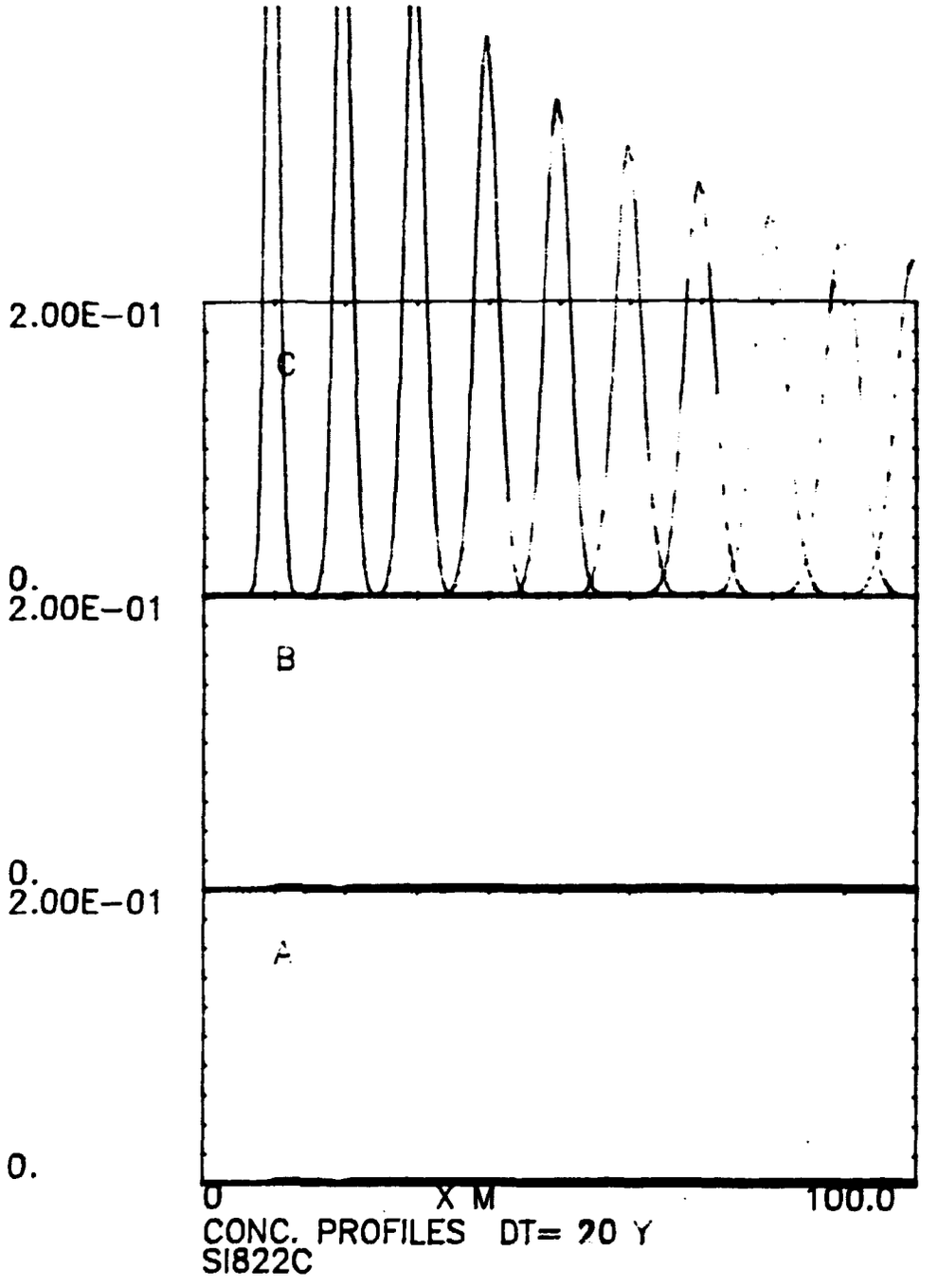

Figure 8-6. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.001$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

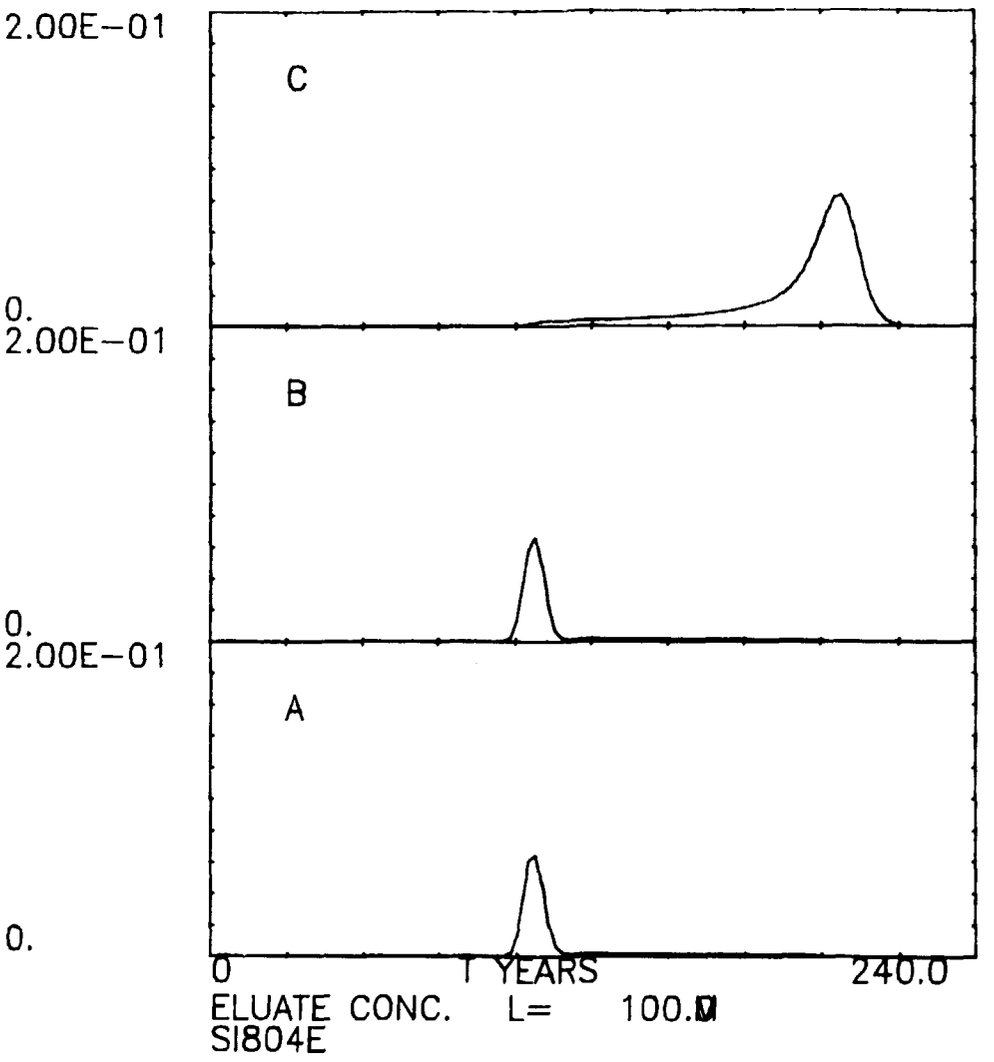

Figure 8-7. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

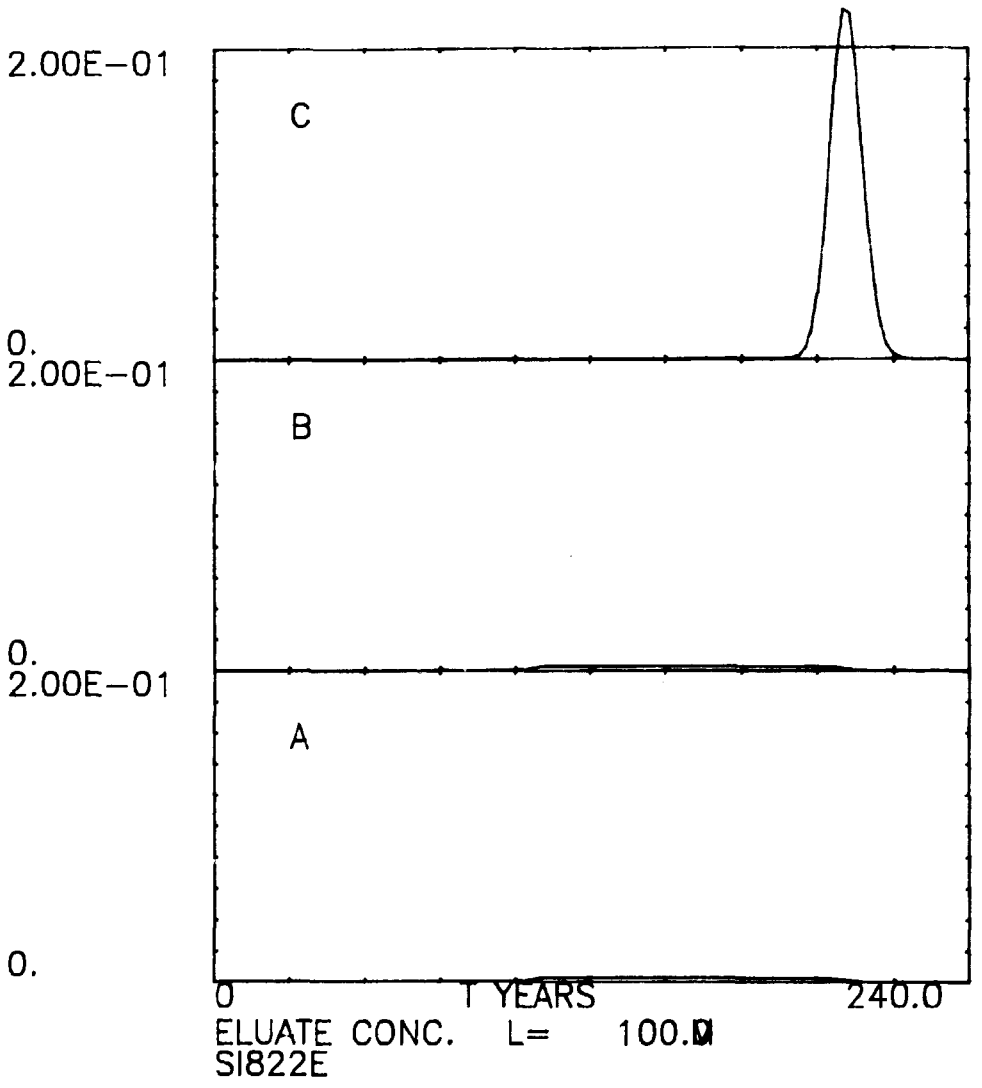

Figure 8-8. $R_f(A)=R_f(B)=1$, $R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

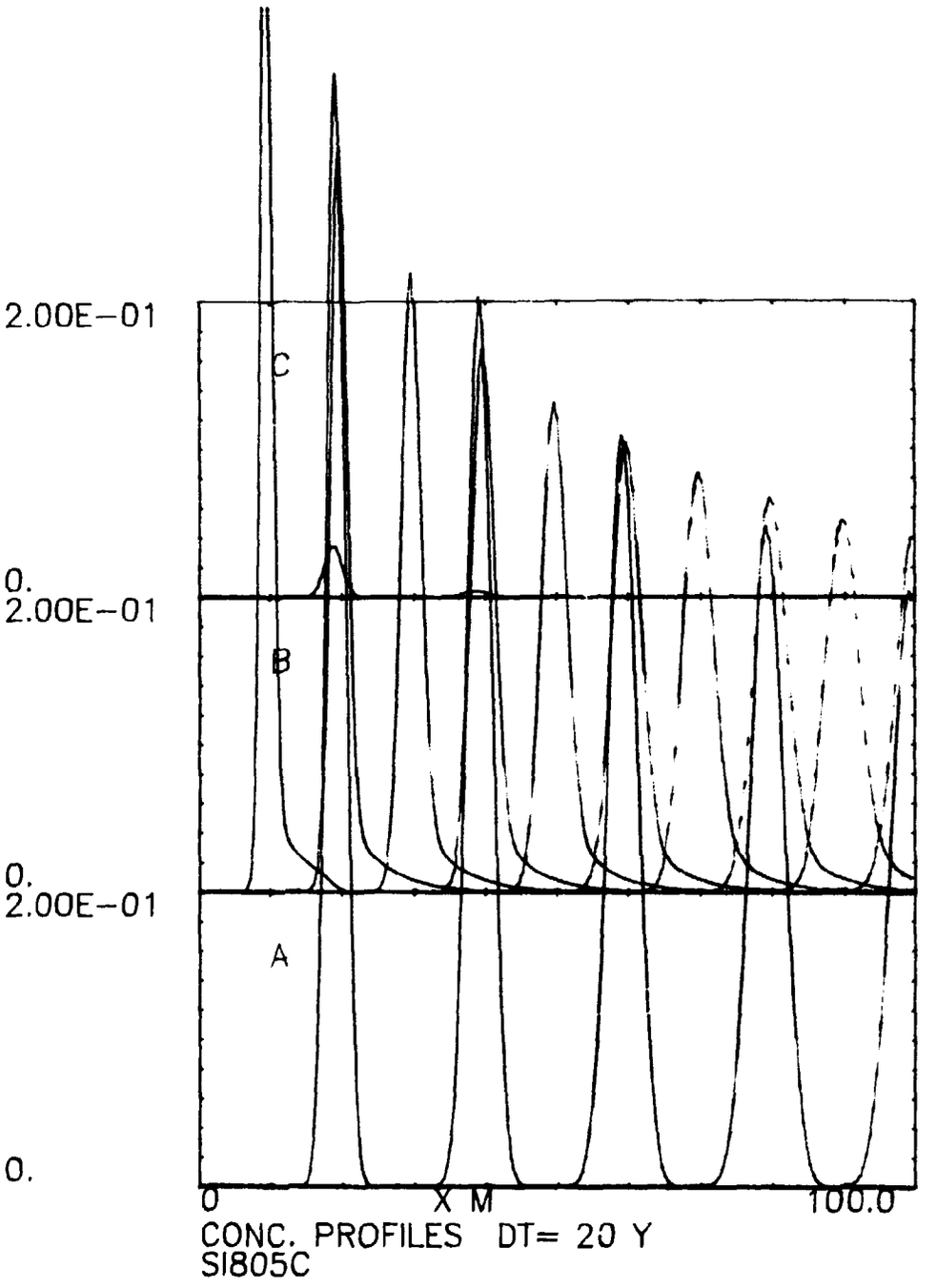

Figure 8-9. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.1$ y^{-1}.

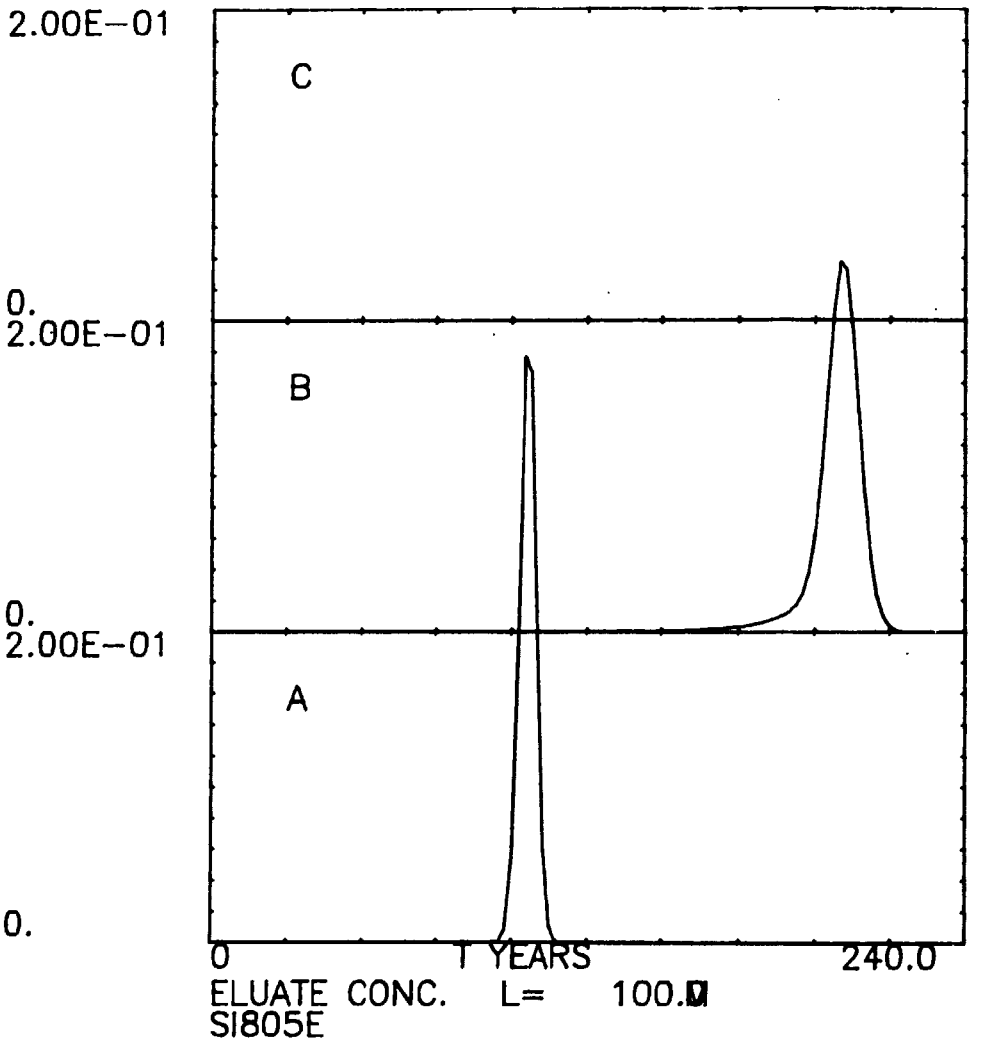

Figure 8-10. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.1$ y^{-1}.

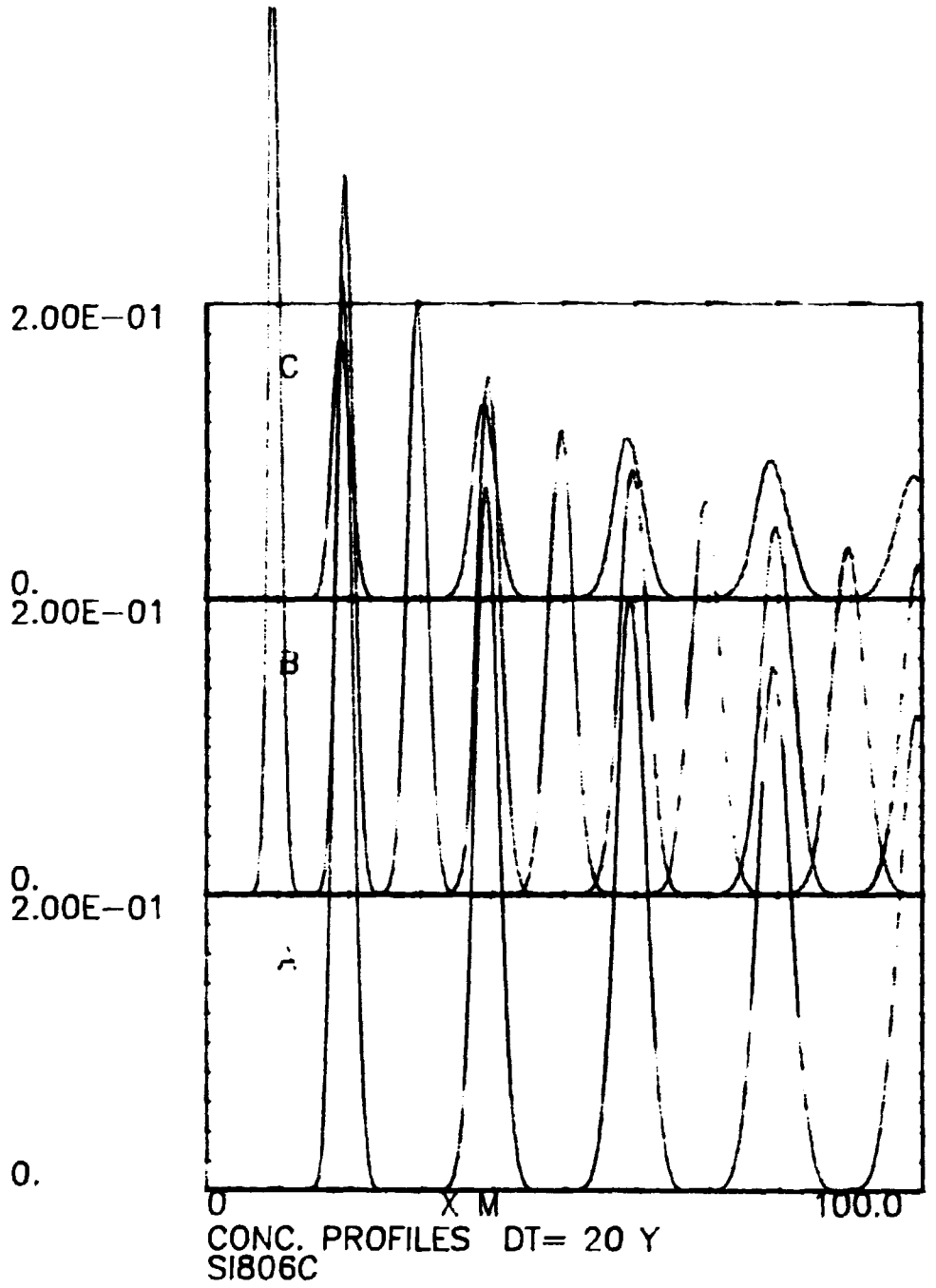

Figure 8-11. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

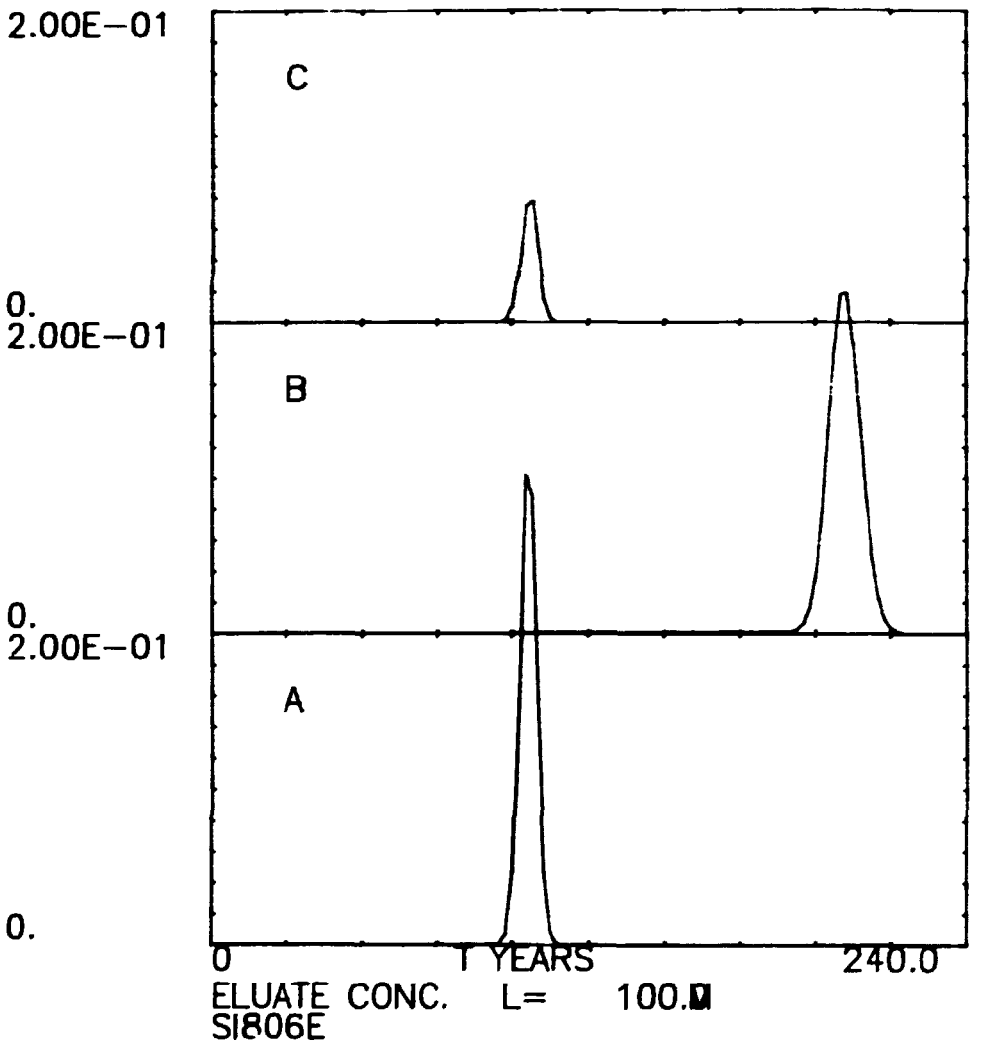

Figure 8-12. $R_f(A)=R_f(C)=1$, $R_f(B)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

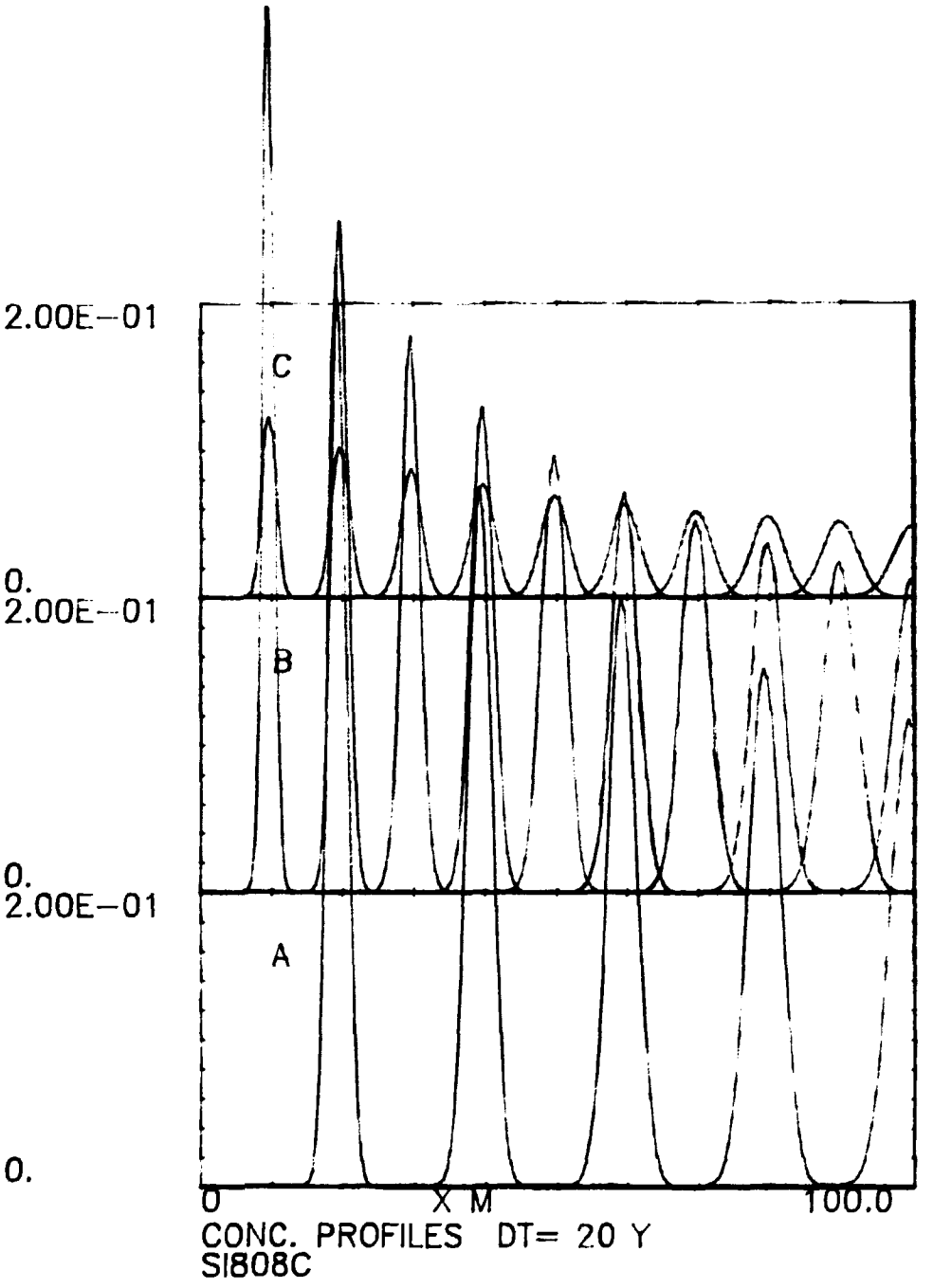

Figure 8-13. $R_f(A)=1$, $R_f(B)=R_f(C)=2$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

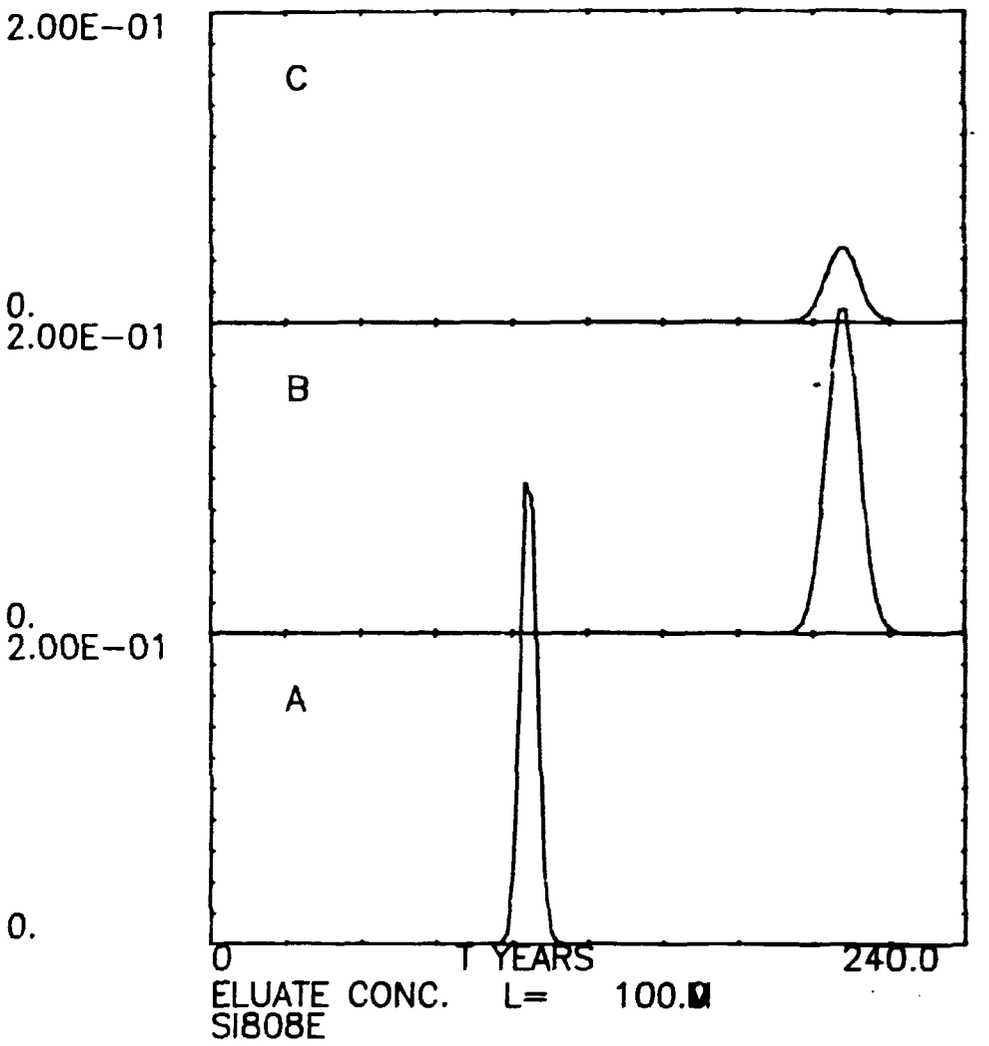

Figure 8-14. $R_f(A)=1$, $R_f(B)=R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

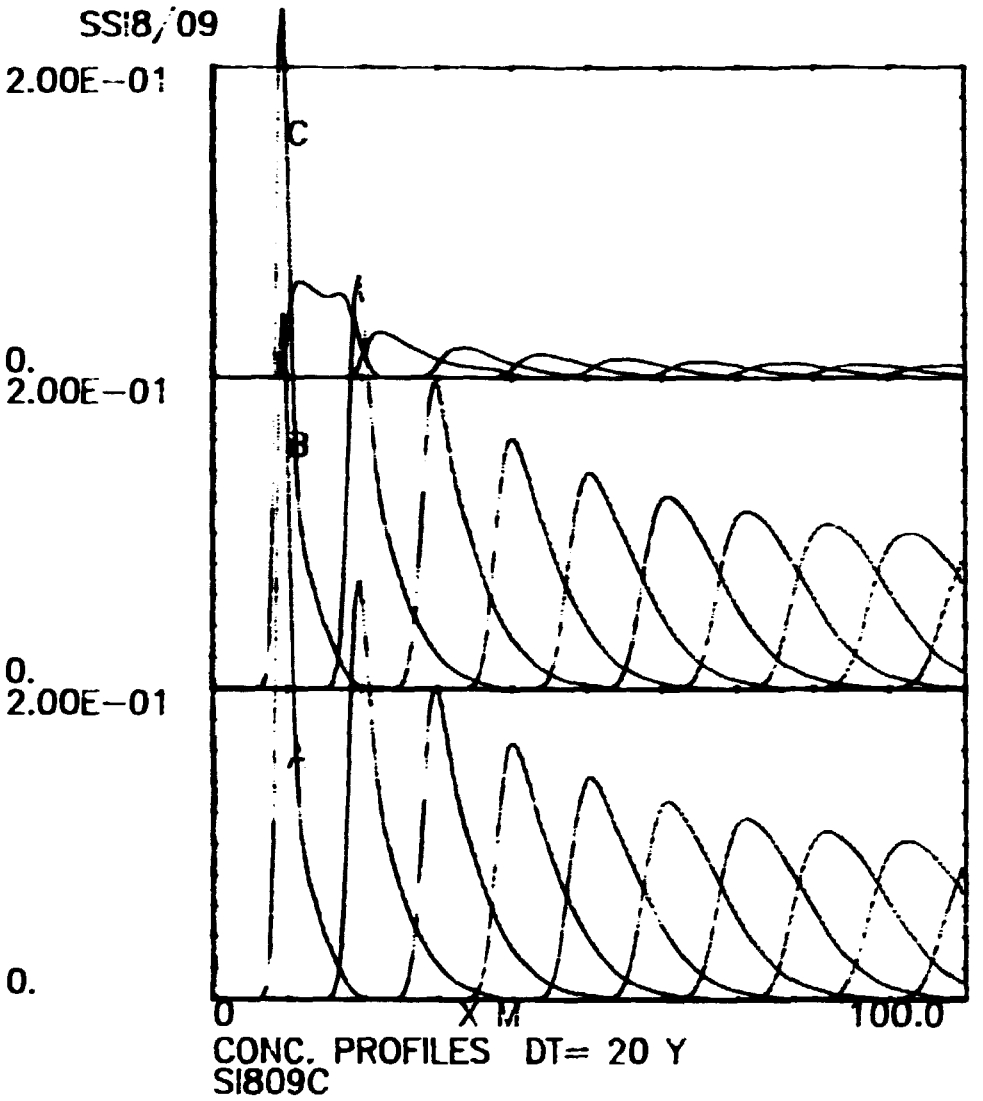

Figure 8-15. $R_f(A)=R_f(B)=2$, $R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-1}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.1$ y^{-1}.

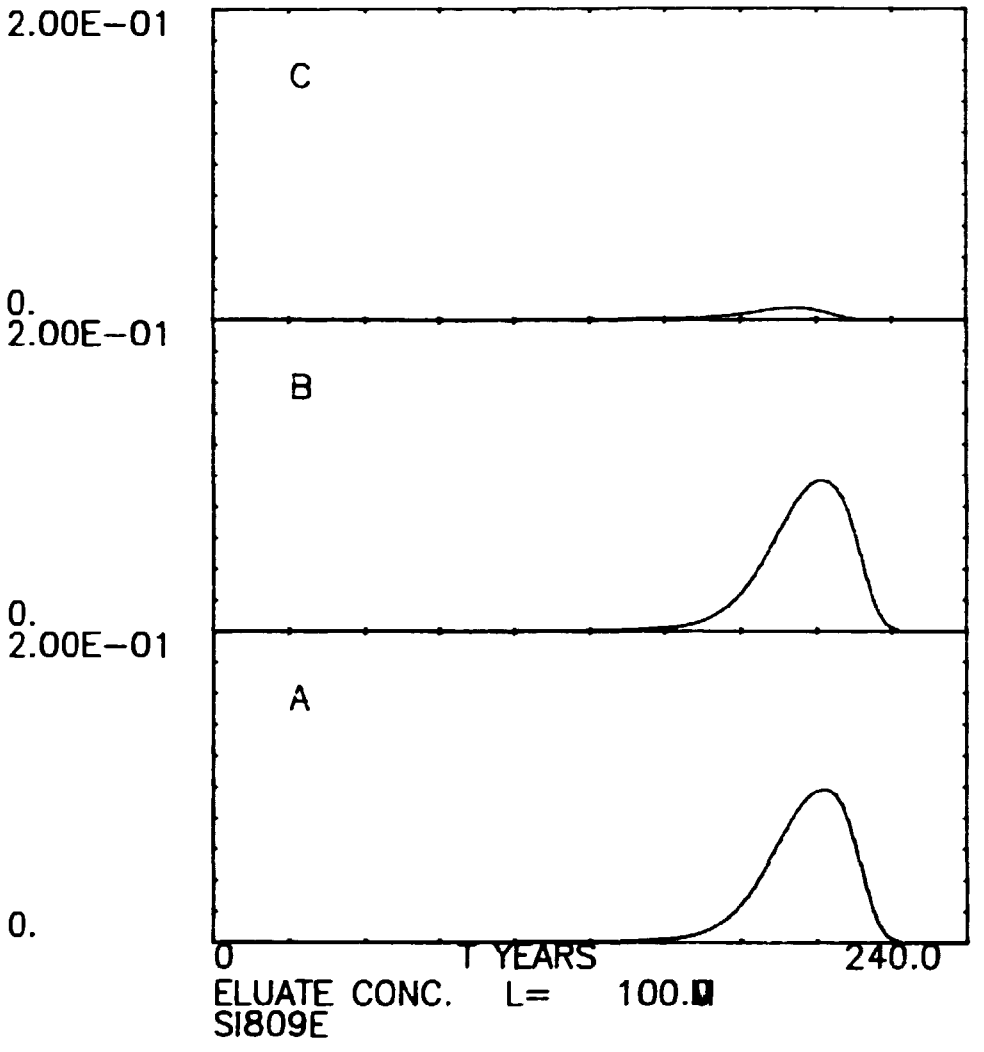

Figure 8-16. $R_f(A)=R_f(B)=2$, $R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-1}, k_1=0.1 $M^{-1}y^{-1}$, k_{-1}=0.1 y^{-1}.

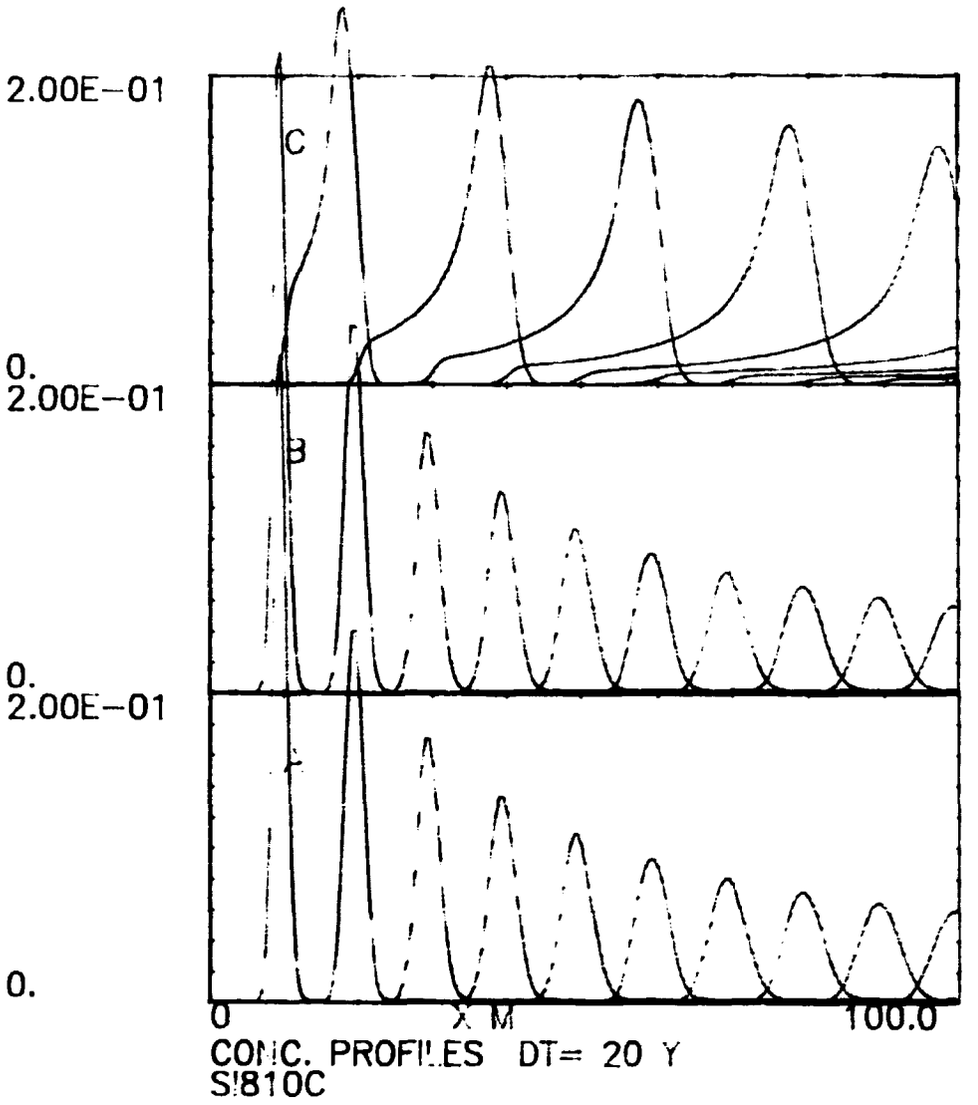

Figure 8-17. $R_{f(A)}=R_f(B)=2$, $R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ $m^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

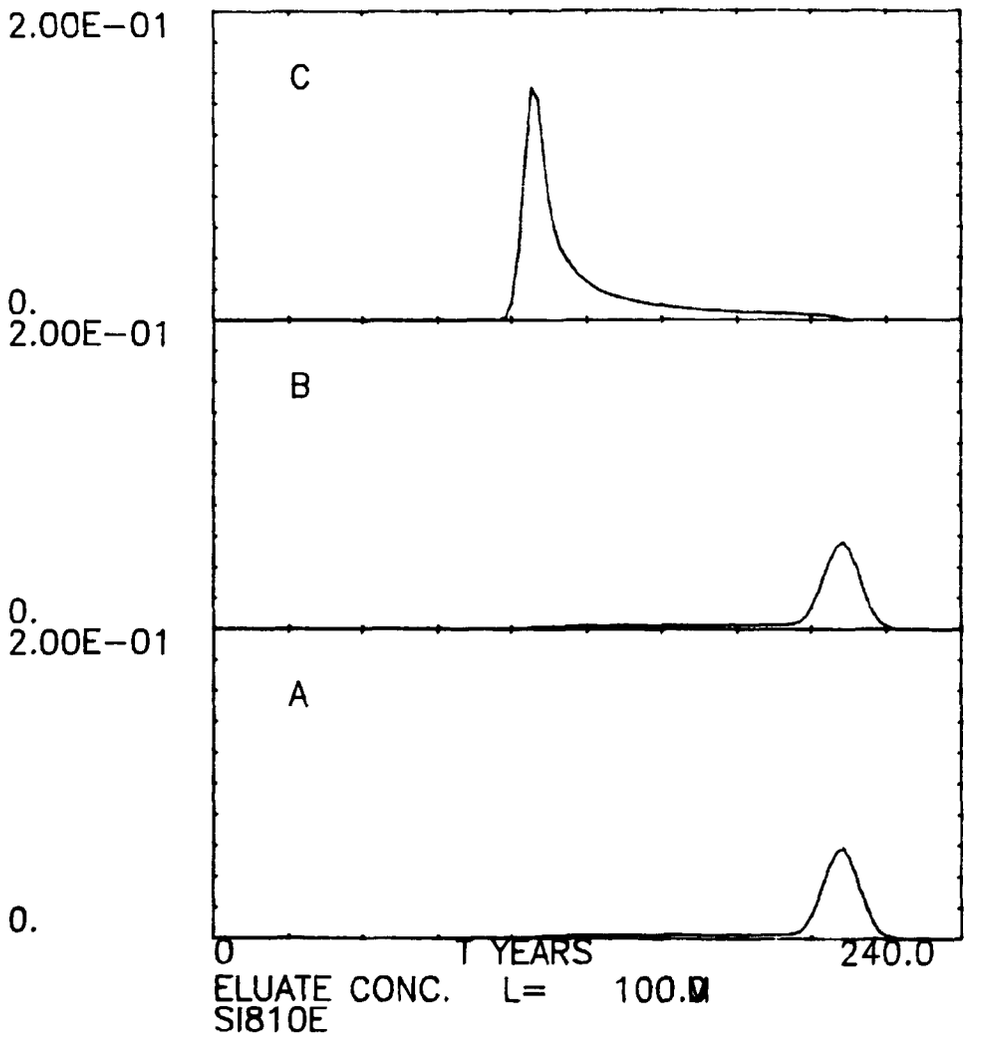

Figure 8-18. $R_f(A)=R_f(B)=2$, $R_f(C)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-1}, $k_1=0.1$ $m^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

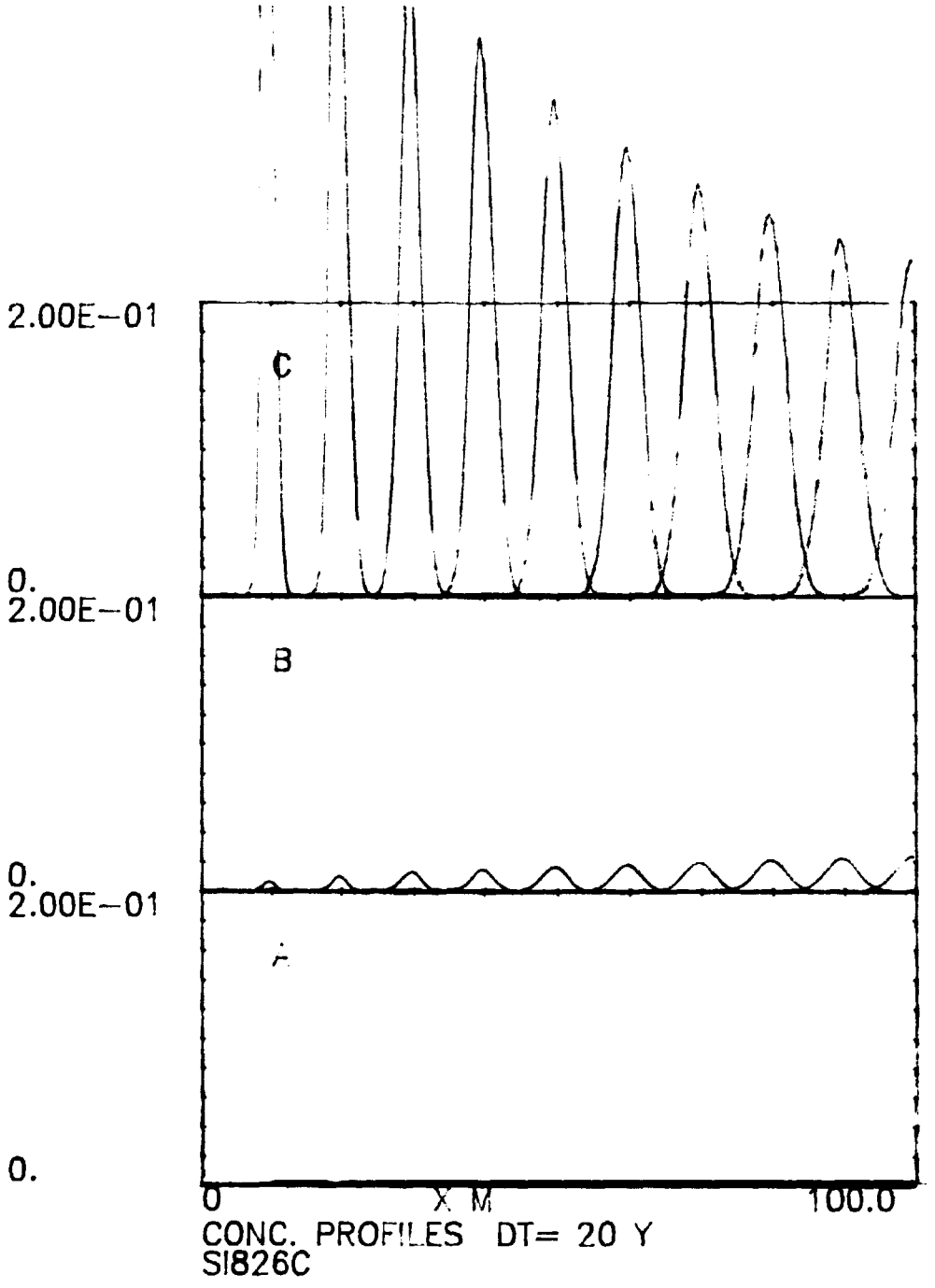

Figure 8-19. $R_f(A)=1$, $R_f(B)=R_f(C)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

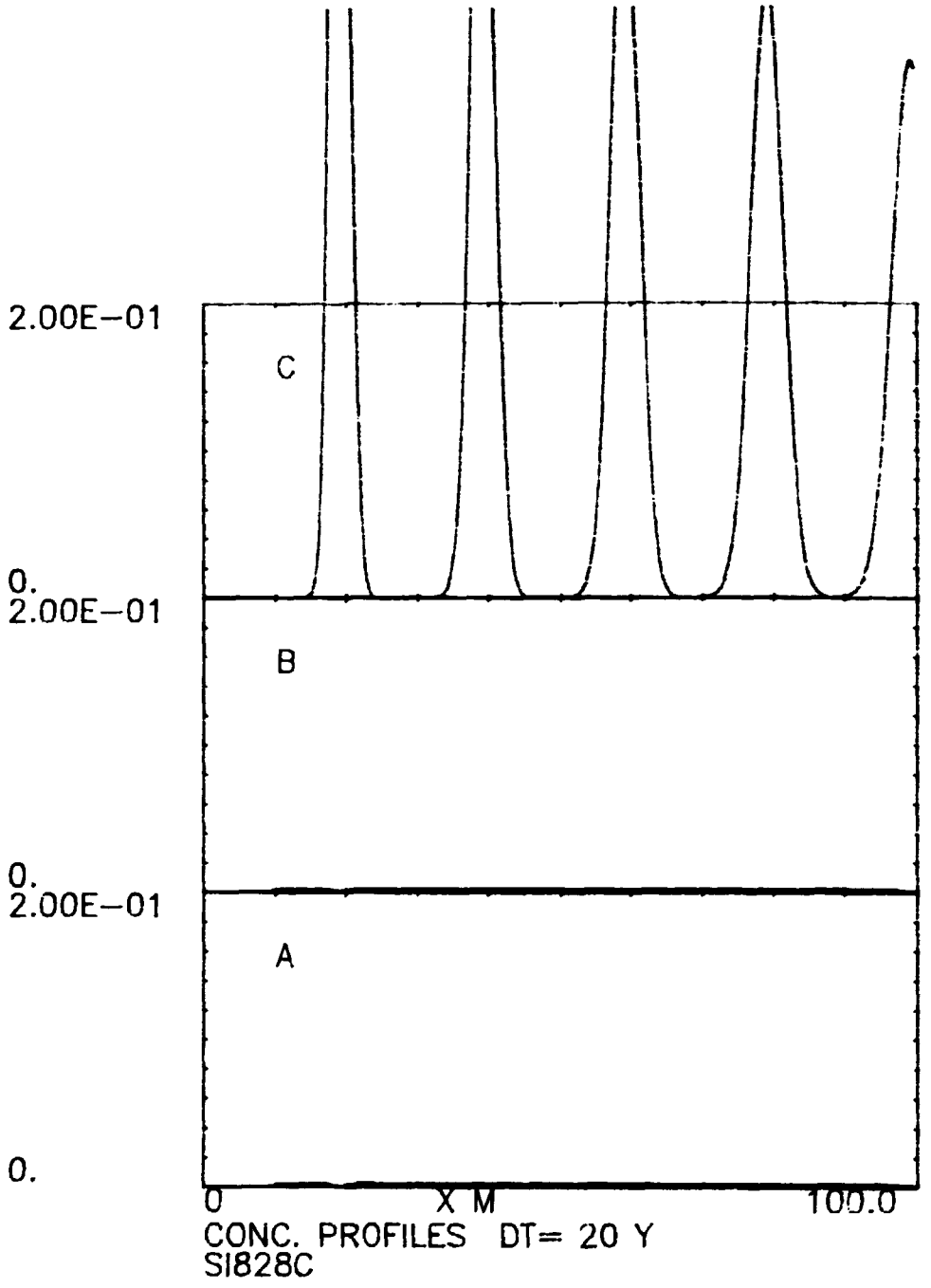

Figure 8-20. $R_f(A)=R_f(B)=2$, $R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

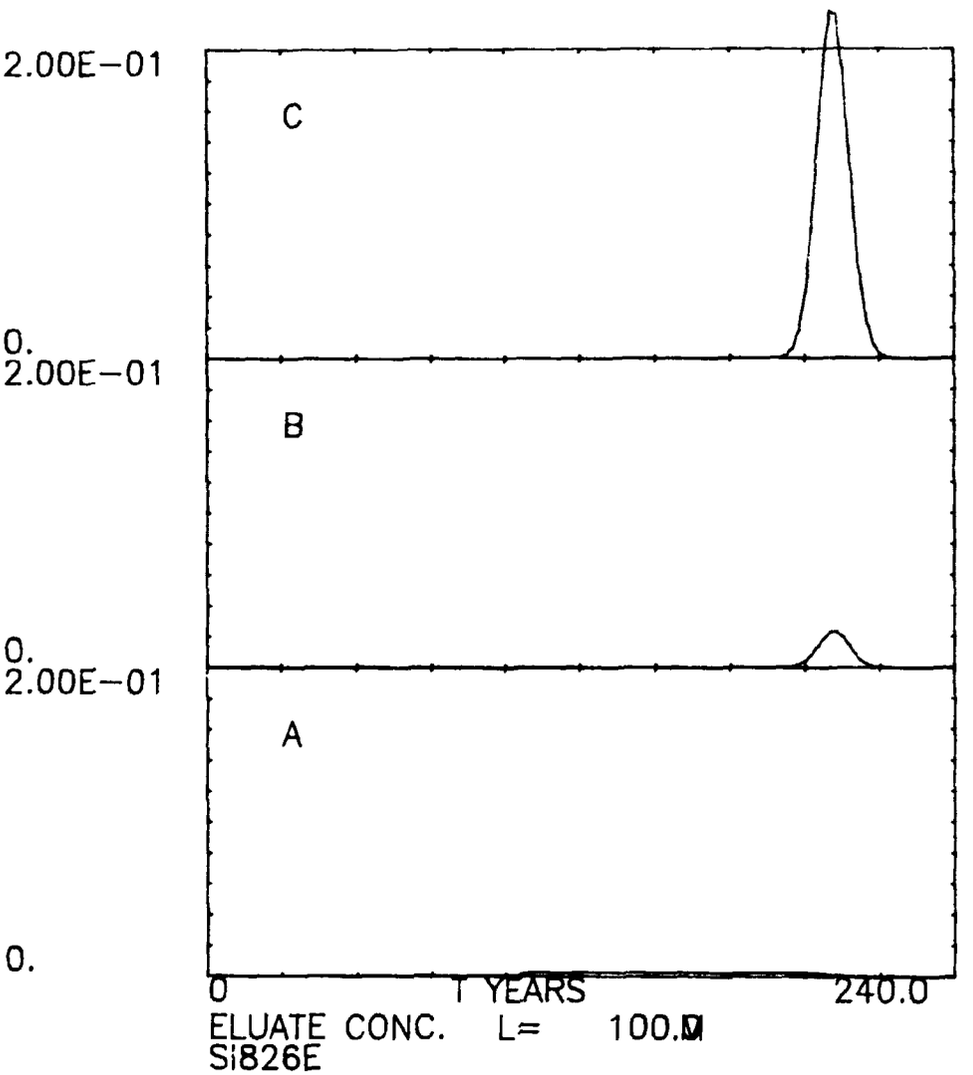

Figure 8-21. $R_f(A)=1$, $R_f(B)=R_f(C)=2$' $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

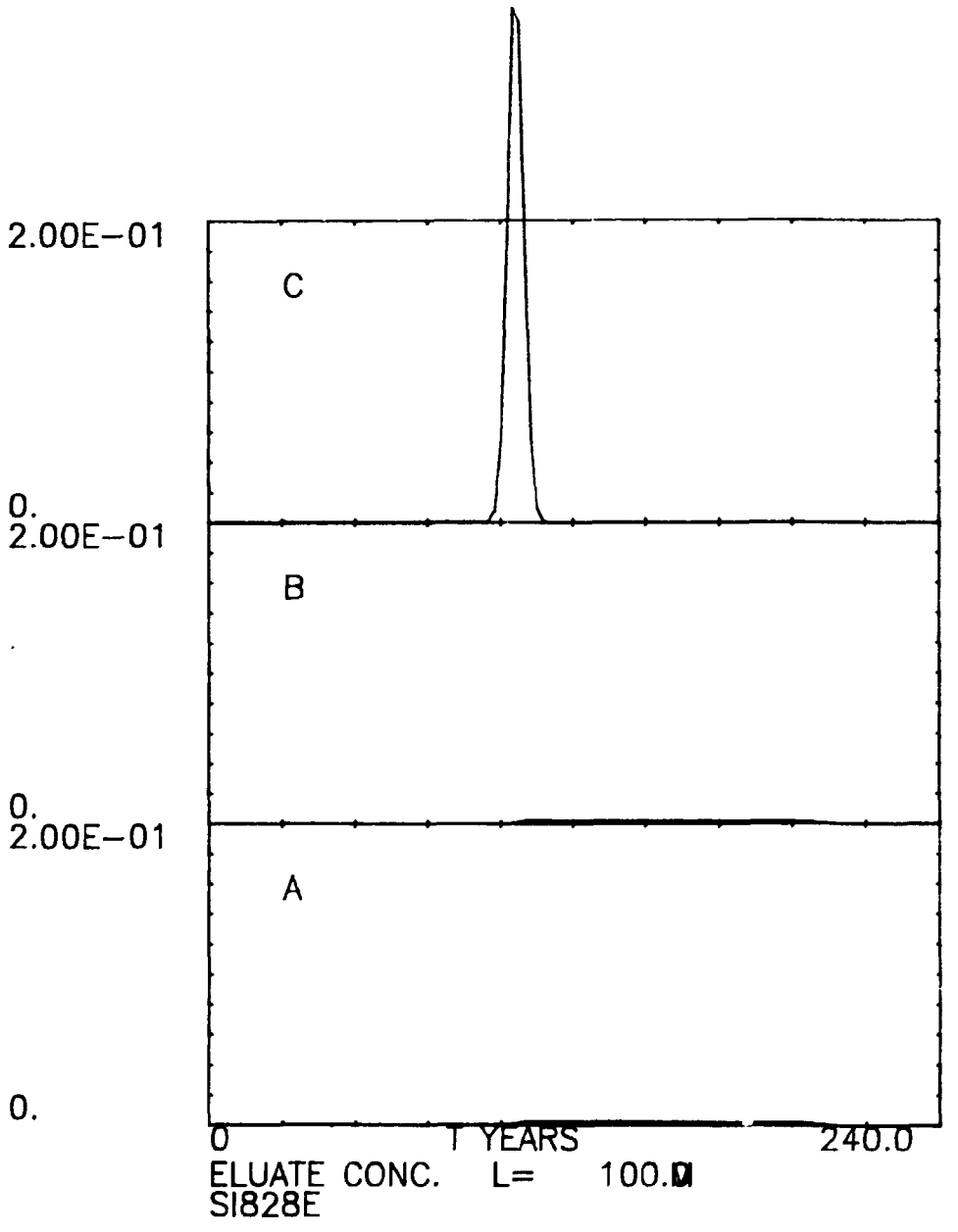

Figure 8-22. $R_f(A)=R_f(B)=2$, $R_f(C)=1$, V=1 m y^{-1}, D=0.03 m y^{-1}, $k_1=0.1$ $M^{-1}y^{-1}$, $k_{-1}=0.001$ y^{-1}.

FIGURES FOR SECTION 4.9

$$A+B \rightleftarrows C+D$$

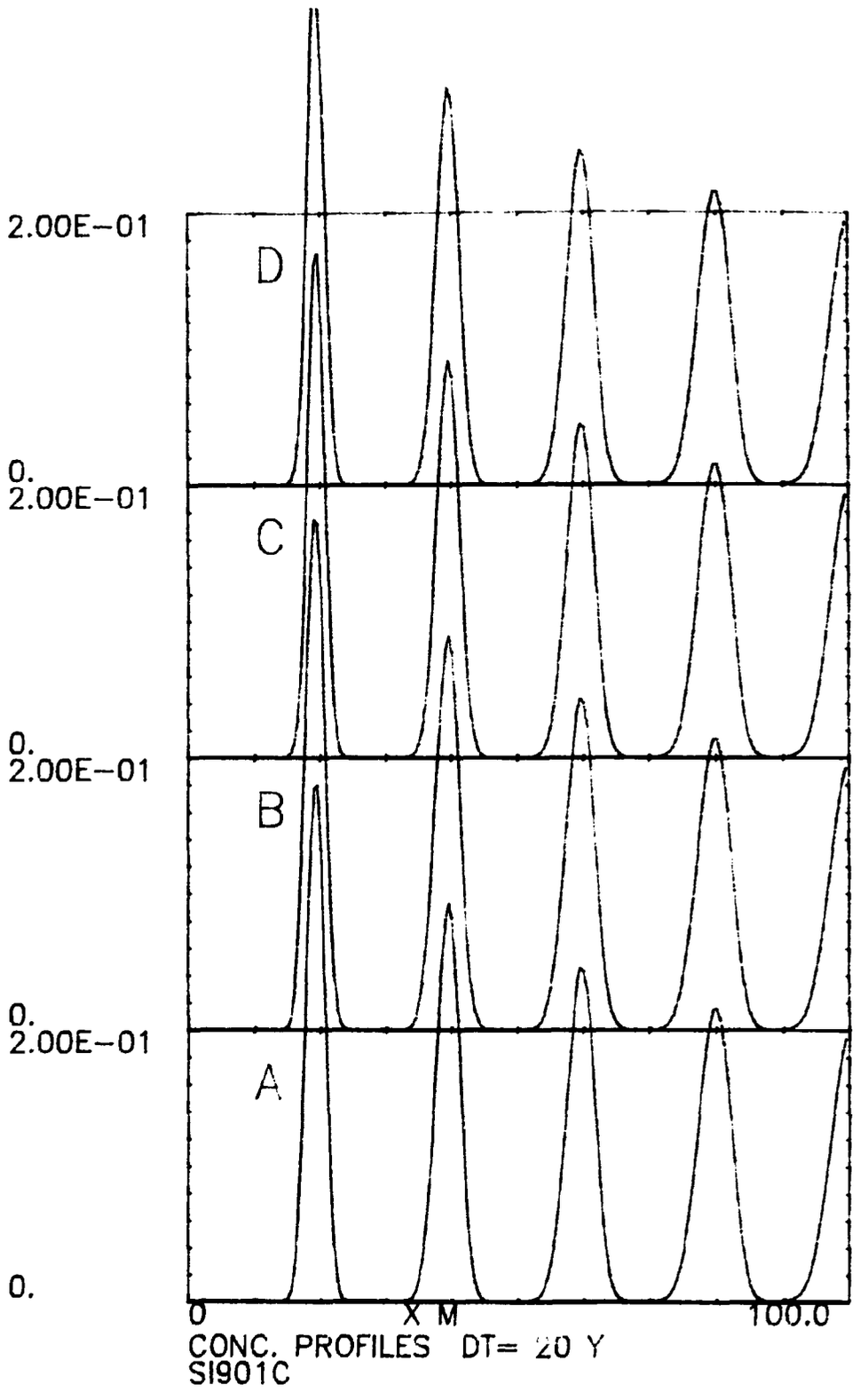

Figure 9-1. $R_f(A)=R_f(B)=R_f(C)=R_f(D)=1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ $M^{-1}y^{-1}$.

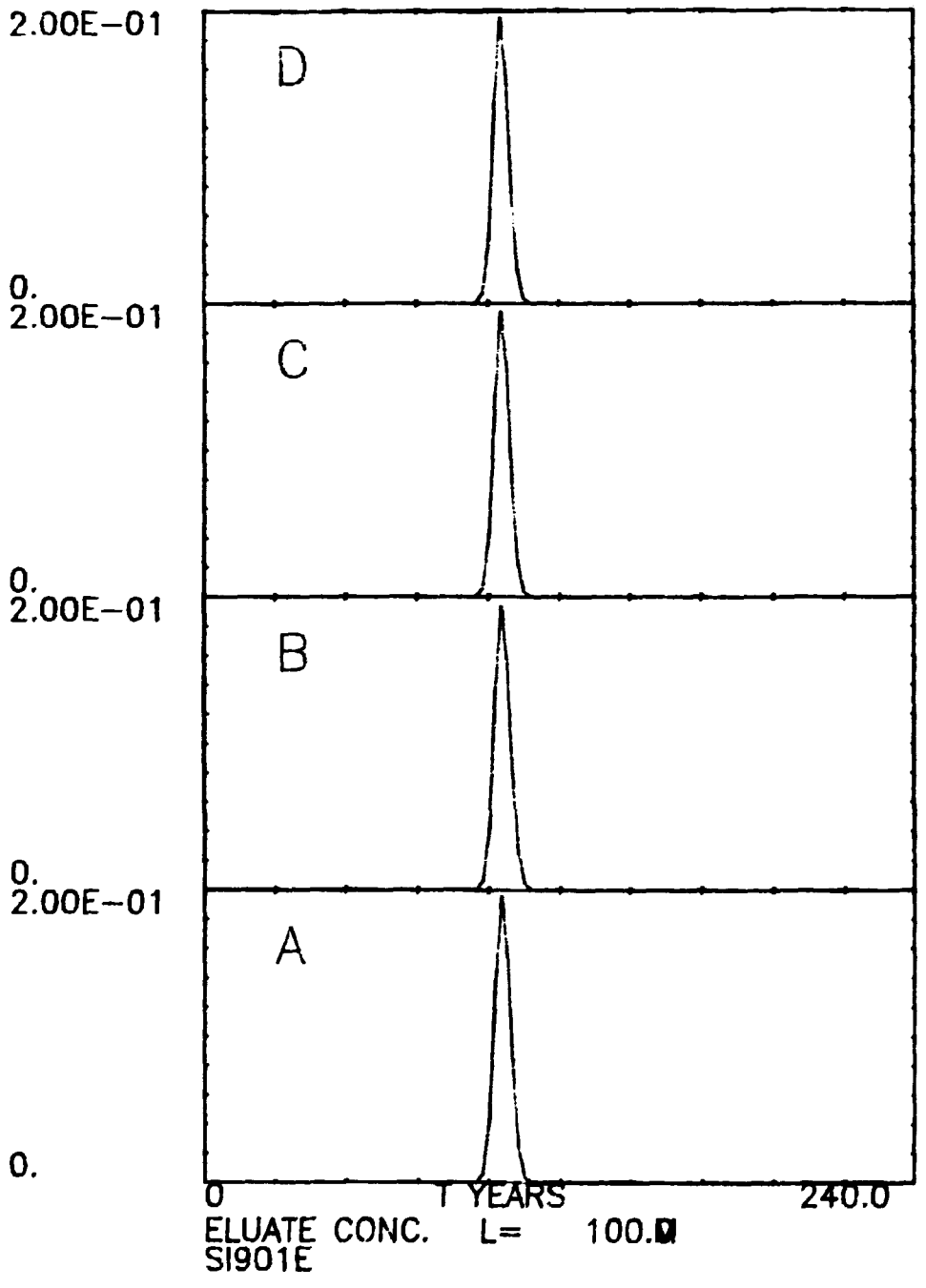

Figure 9-2. $R_f(A)=R_f(B)=R_f(C)=R_f(D)= 1$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ $M^{-1}y^{-1}$.

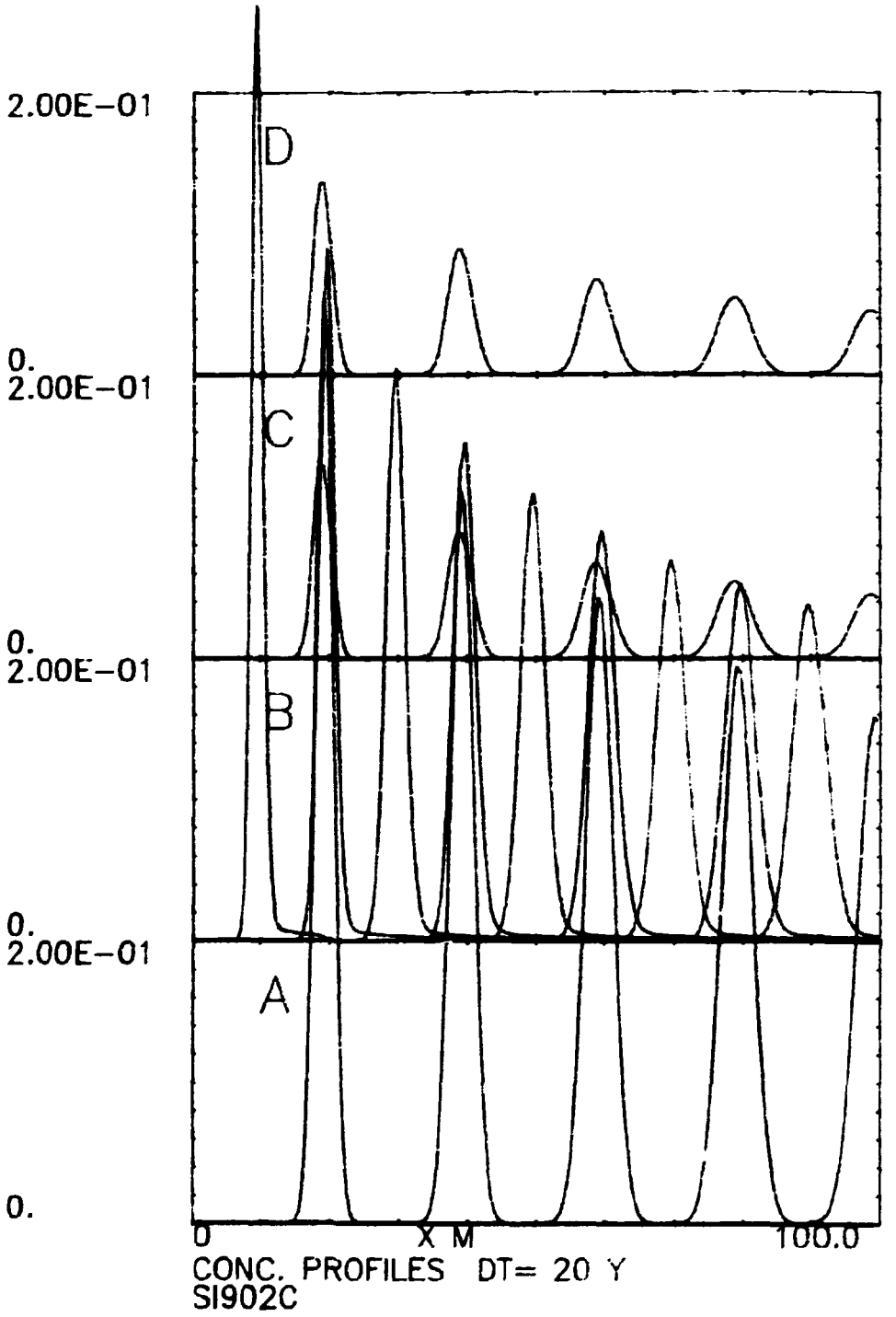

Figure 9-3. $R_f(A)=R_f(C)=R_f(D)=1$, $R_f(B)=2$, $V=1\ m\ y^{-1}$, $D=0.03\ m\ y^{-2}$, $k_1=k_{-1}=0.1\ M^{-1}y^{-1}$.

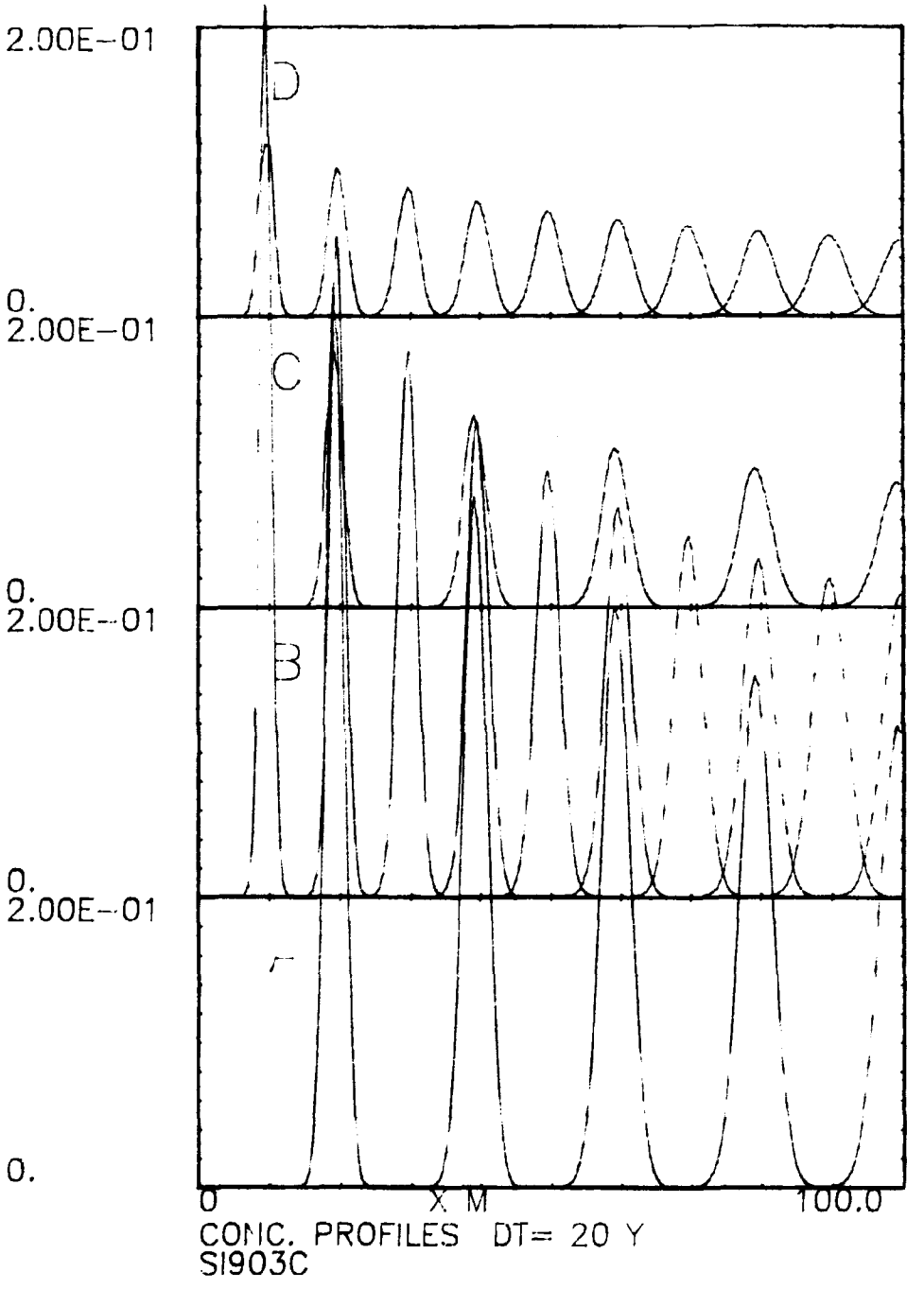

Figure 9-4. $R_f(A)=R_f(C)=1$, $R_f(B)=R_f(D)=2$, $V=1\ m\ y^{-1}$, $D=0.03\ m\ y^{-2}$, $k_1=k_{-1}=0.1\ M^{-1}y^{-1}$.

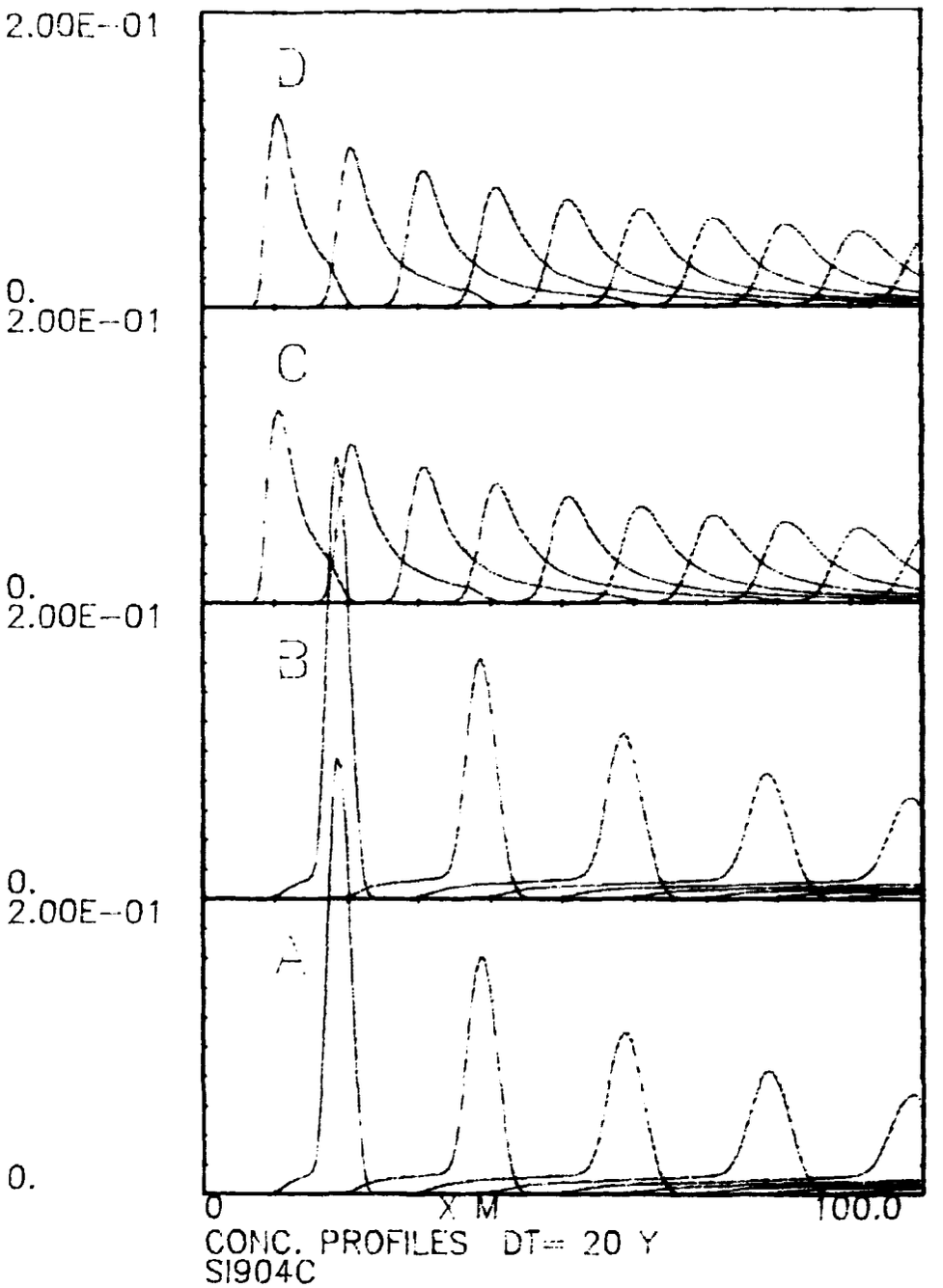

Figure 9-5. $R_f(A)=R_f(B)=1$, $R_f(C)=R_f(D)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ $M^{-1}y^{-1}$.

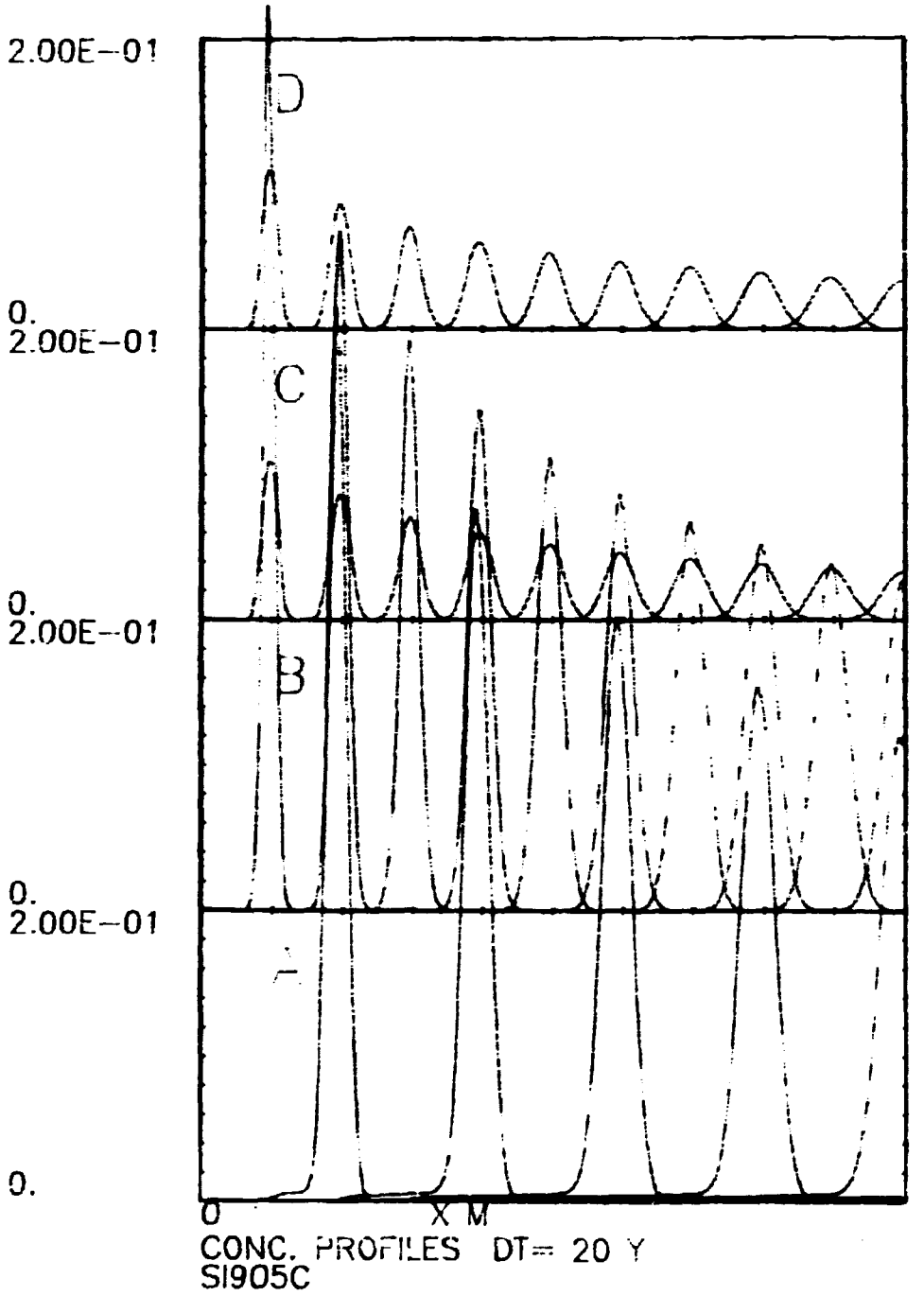

Figure 9-6. $R_f(A)=1$, $R_f(B)=R_f(C)=R_f(D)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ $M^{-1}y^{-1}$.

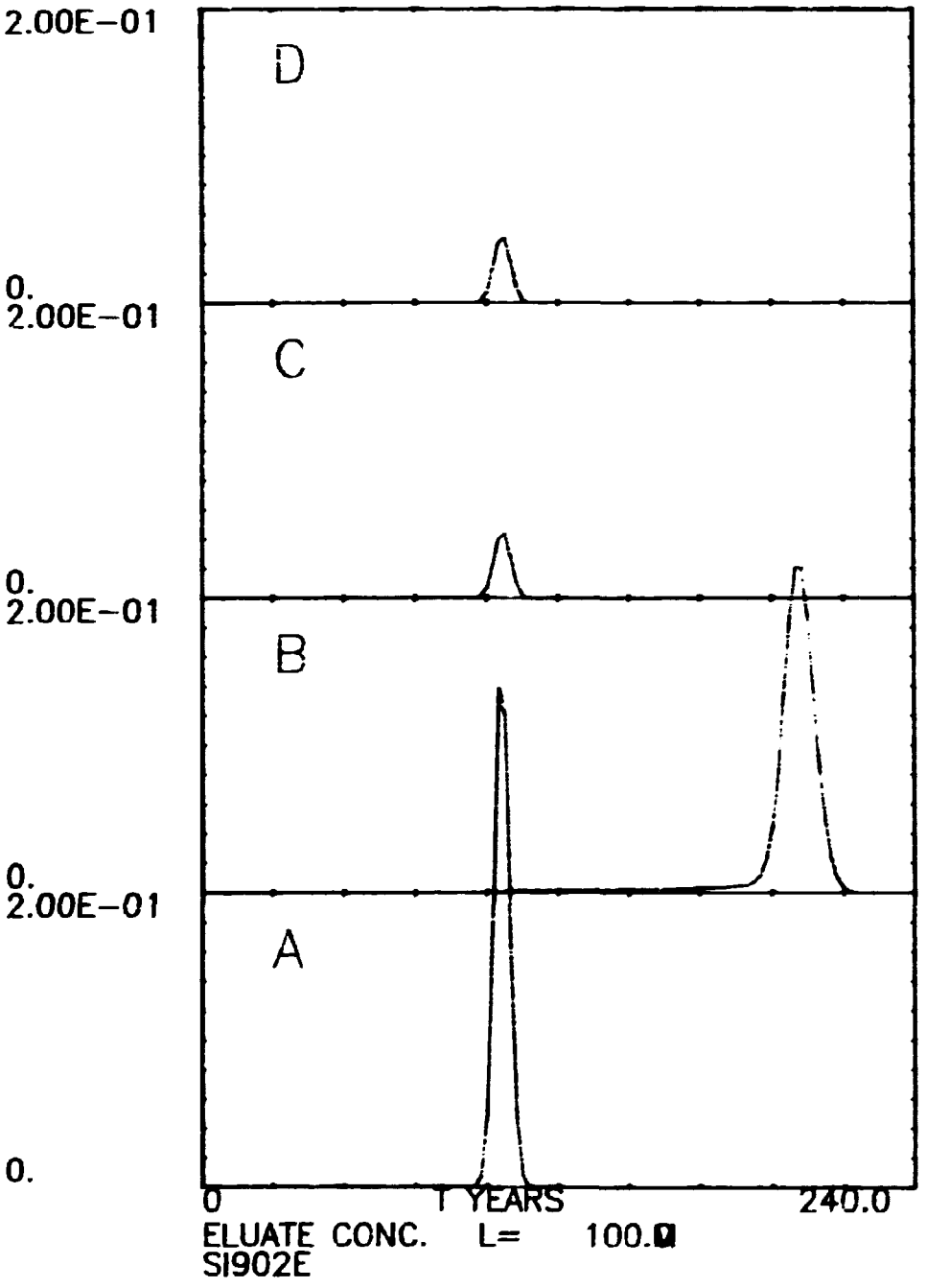

Figure 9-7. $R_f(B)=2$, $R_f(A)=R_f(C)=R_f(D)$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ $M^{-1}y^{-1}$.

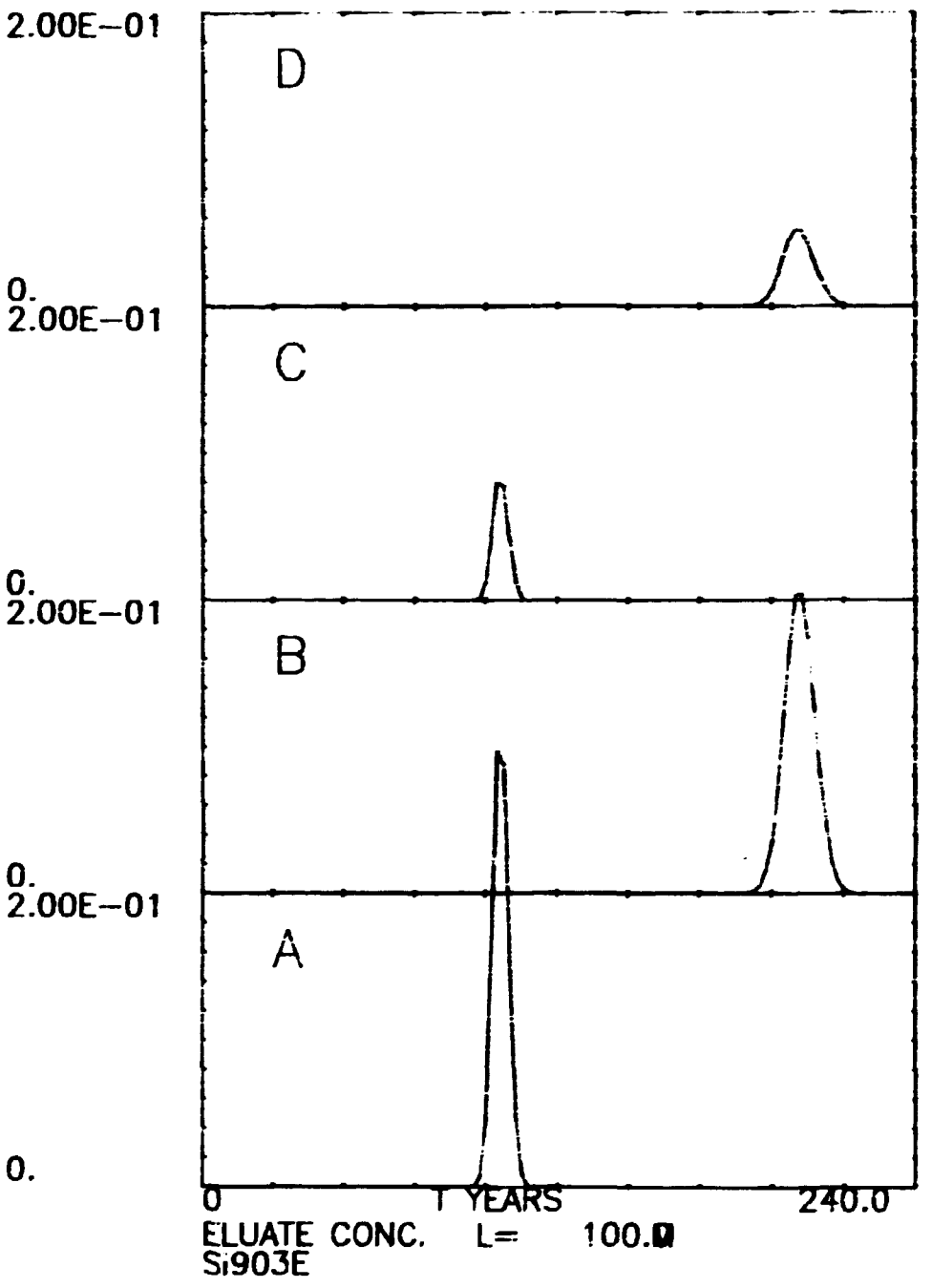

Figure 9-8. $R_f(A)=R_f(C)=1$, $R_f(B)=R_f(D)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ $M^{-1}y^{-1}$.

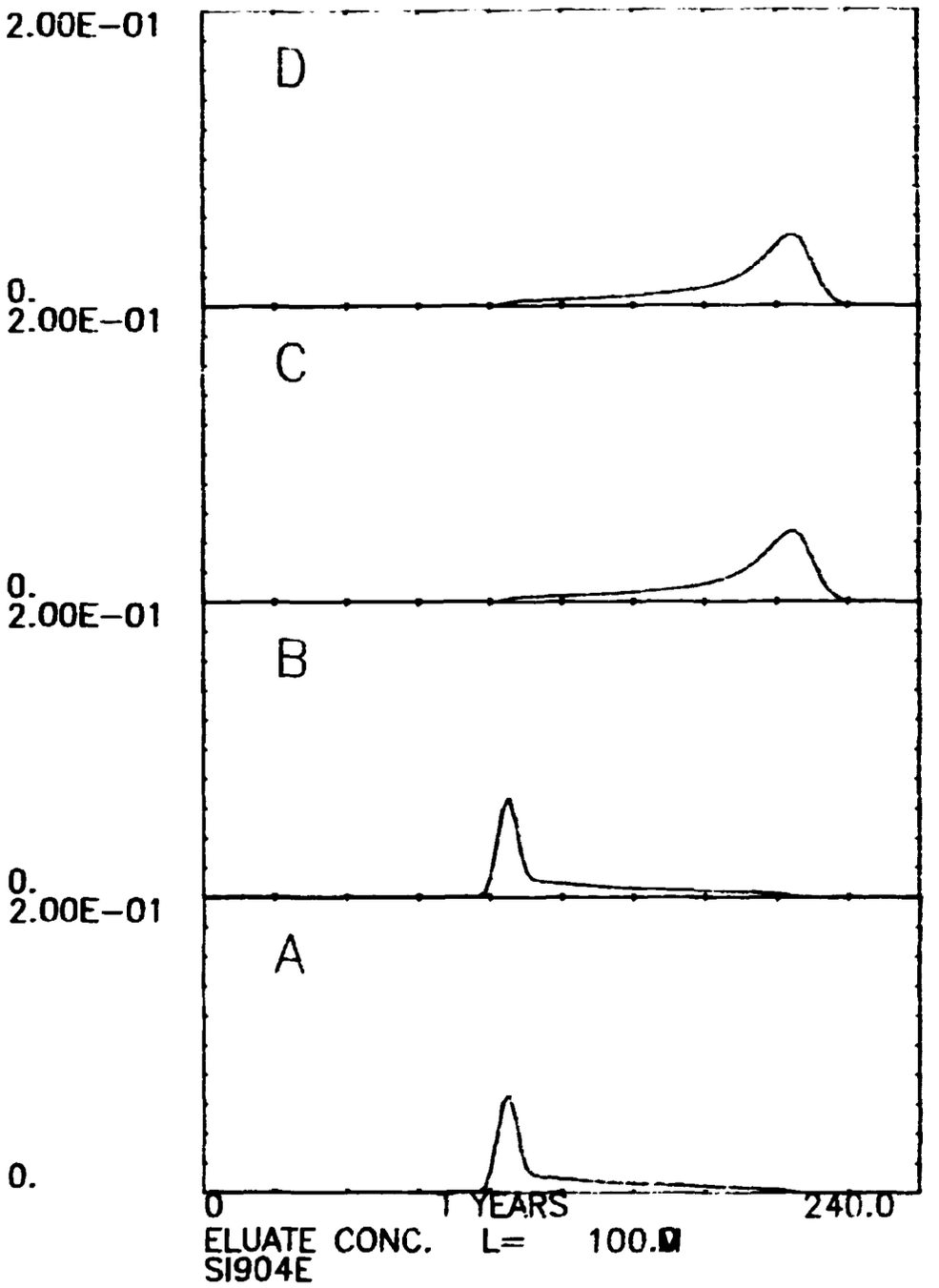

Figure 9-9. $R_f(A)=R_f(B)=1$, $R_f(C)=R_f(D)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ $M^{-1}y^{-1}$.

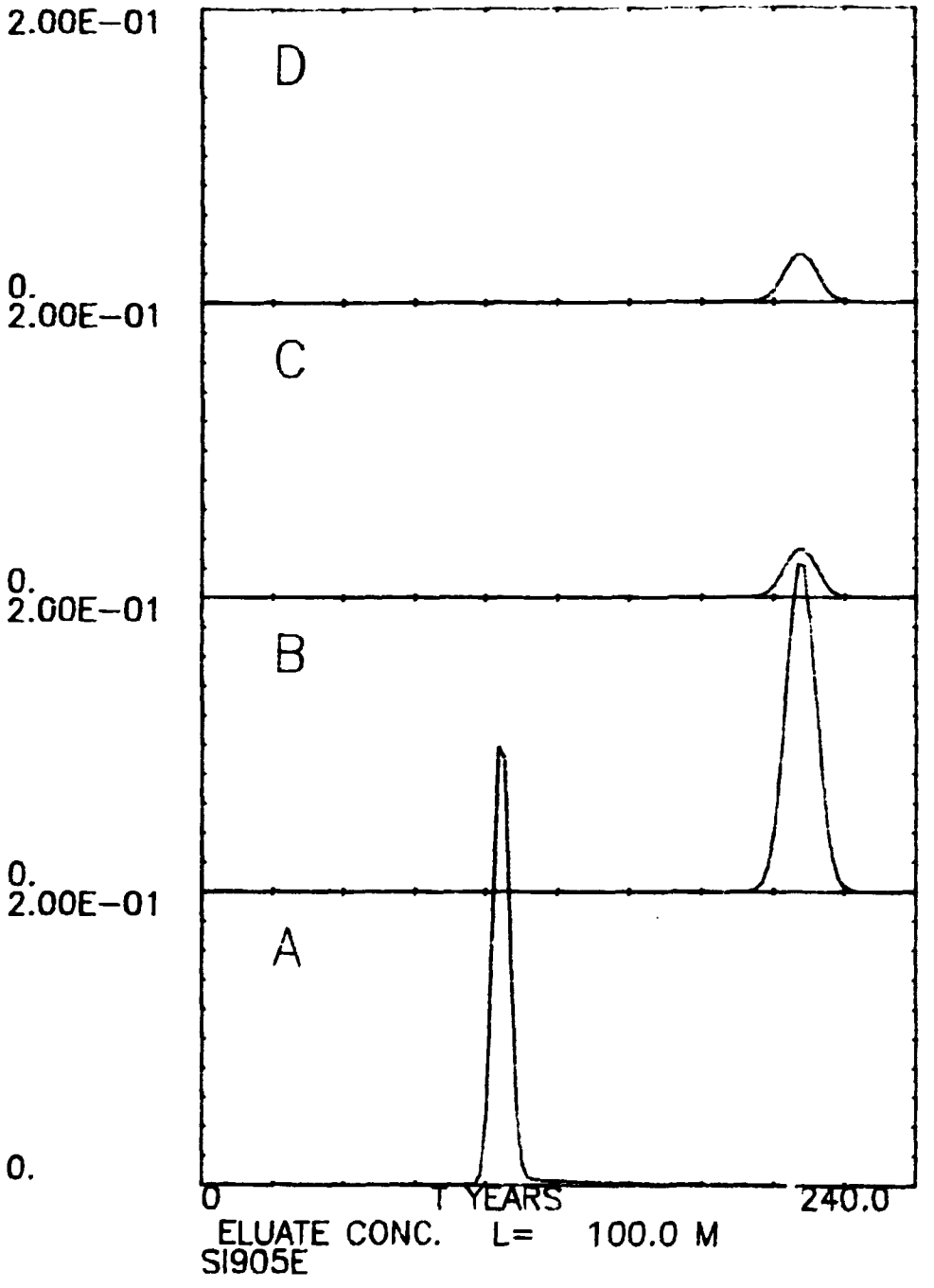

Figure 9-10. $R_f(A)=1$, $R_f(B)=R_f(C)=R_f(D)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.1$ $M^{-1}y^{-1}$.

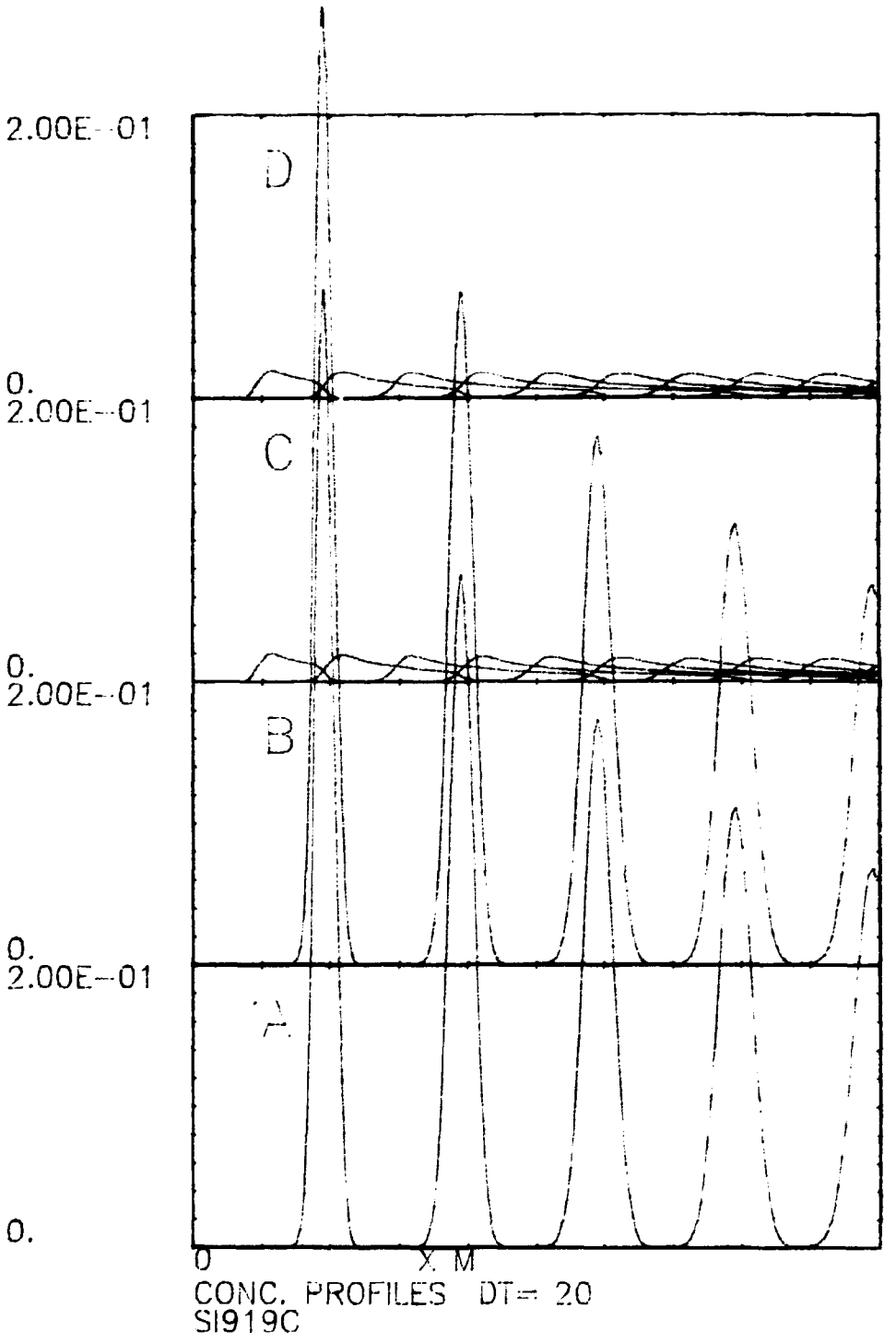

Figure 9-11. $R_f(A)=R_f(B)=1$, $R_f(C)=R_f(D)=2$, $V=1\ m\ y^{-1}$, $D=0.03\ m\ y^{-2}$, $k_1=k_{-1}=0.01\ M^{-1}y^{-1}$.

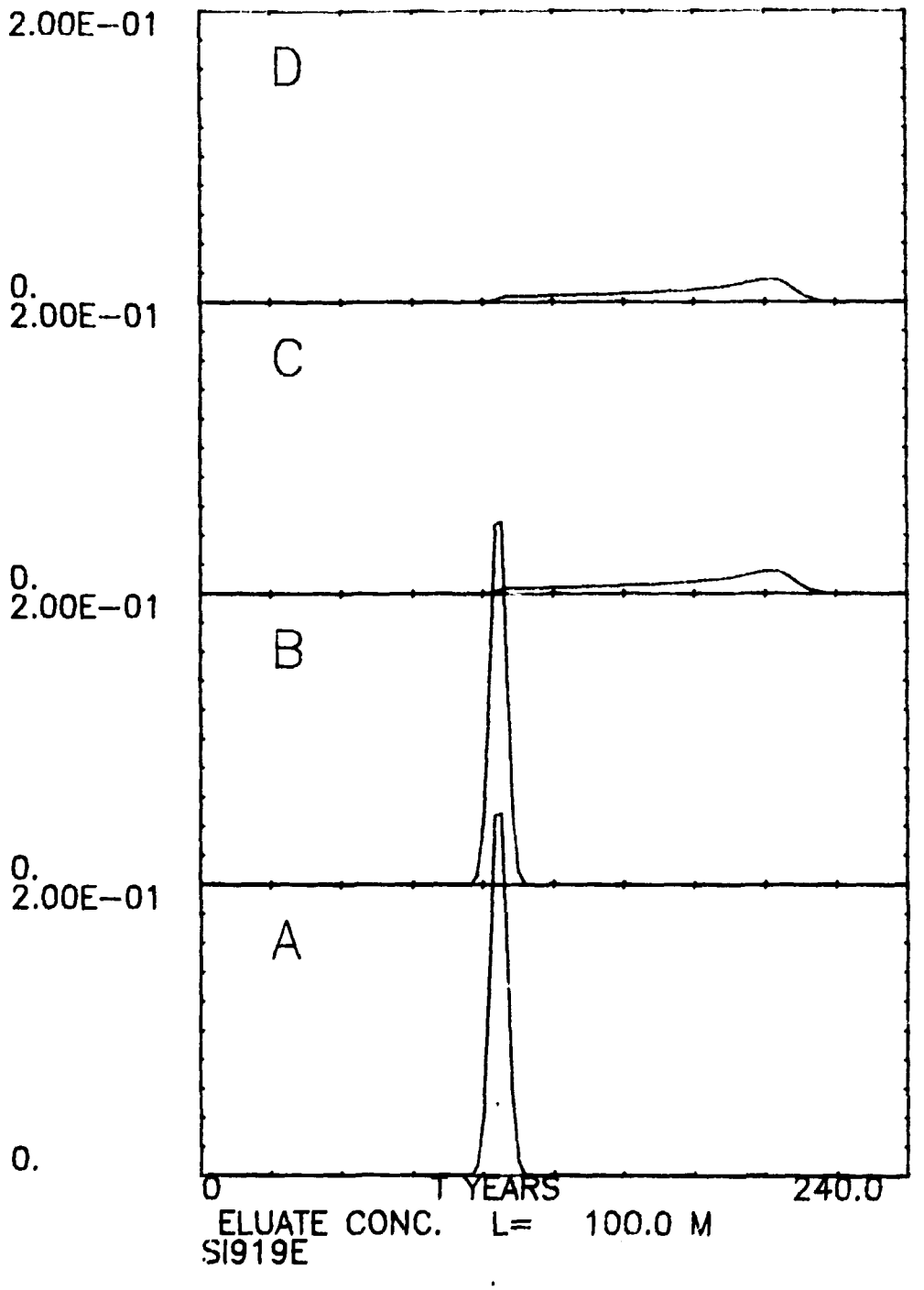

Figure 9-12. $R_f(A)=R_f(B)=1$, $R_f(C)=R_f(D)=2$, $V=1$ m y^{-1}, $D=0.03$ m y^{-2}, $k_1=k_{-1}=0.01$ $M^{-1}y^{-1}$.

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Title and author(s)

The influence of chemical reactions on the mobility of radionuclides in the terrestrial enviroment.

Lars Carlsen, Ole John Nielsen, Peter Bo, and Conny Ditlevsen

Date February 1986

Department or group

Chemistry Department

Group's own registration number(s)

163 pages + 1 tables + 124 illustrations

Abstract

The influence of the kinetics of chemical and physico-chemical reactions on the mobility of radionuclides in the terrestrial environment has been studied theoretically by application of the COLUMN2 computer code. A variety of reaction systems has been analyzed comprising:

$A \rightarrow B$

$A \rightarrow B \rightarrow C$

$A \underset{\rightarrow}{\overset{\rightarrow}{\ddagger}} B$

$A \underset{\rightarrow}{\overset{\rightarrow}{\ddagger}} B \rightarrow C$

$A \underset{\leftarrow}{\overset{\rightarrow}{\ddagger}} B \underset{\leftarrow}{\overset{\rightarrow}{\ddagger}} C$

$A + X \rightarrow B$

$A + B \underset{\leftarrow}{\overset{\rightarrow}{\ddagger}} C$

$A + B \underset{\leftarrow}{\overset{\rightarrow}{\ddagger}} C + D.$

The study unequivocally discloses the importance of the chemistry in controlling the migration behaviour of pollutants, e.g. radionuclides in the terrestrial environment. The analyses suggest the necessity of studying possible geochemical reaction in detail, including both retention characteristics as well as reaction kinetics. The work has been carried out under contract with the National Institute of Radiation Protection (SSI), Stockholm, Sweden (contract No. P 276-84)

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